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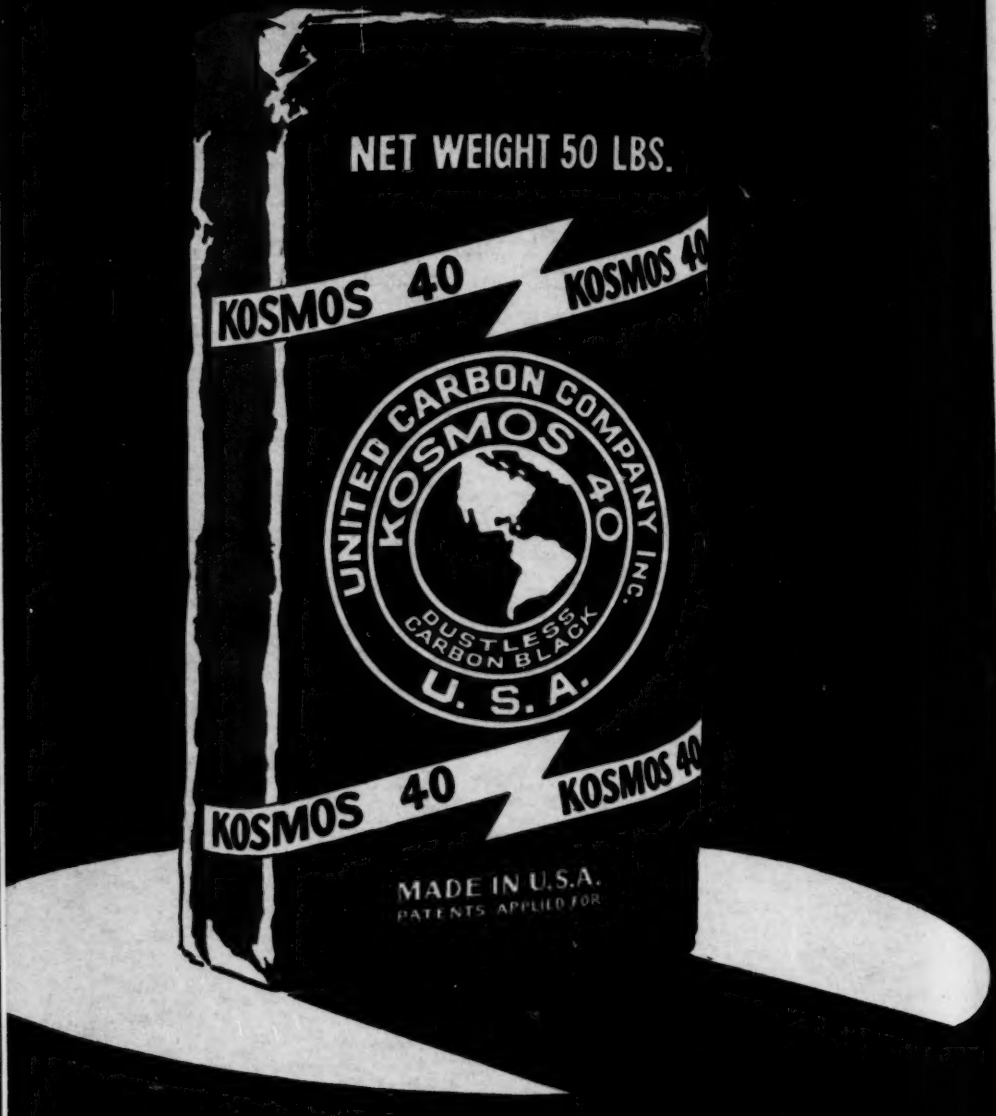
RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XIX NUMBER 3

July, 1946

Published Quarterly under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY
at Prince and Lemon Sts., Lancaster, Pa.



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RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Division of Rubber Chemistry of the American Chemical Society,
Prince and Lemon Streets,
Lancaster, Pa.

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Vol. XIX **July, 1946** **No. 3**

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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A NEW APPROACH TO THE THEORY OF RUBBERLIKE ELASTICITY *

MAURICE L. HUGGINS

KODAK RESEARCH LABORATORIES, ROCHESTER, N. Y.

INTRODUCTION

It is now generally accepted that long-range rubberlike elasticity is an entropy effect, dependent on the possibility of easy rotation about single bonds in giant chain or network molecules[1]. The orientation about these bonds is less random when a sample of rubber or a rubberlike material is in a stretched condition than when it is unstretched (Figure 1).

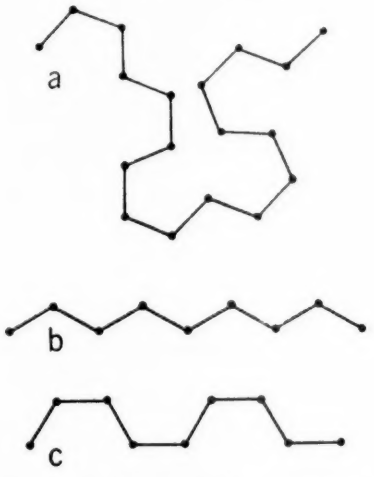


FIG. 1.—(a) An irregularly kinked chain molecule and (b, c) two regular arrangements of the chain atoms. Stretching favors b or c over a.

Various attempts have been made to connect the macroscopic properties (stress-strain curves) of such materials with specific structural models. At first, the substance was assumed to be composed of many long-chain molecules, with (for simplicity) perfectly free rotation about each of the chain bonds. On this basis relationships were derived connecting the initial elastic modulus, chain length and other molecular constants (bond distances and angles), and temperature[2].

The direct proportionality between the elastic modulus and the absolute temperature, arrived at in this way, agrees with experimental results on

* Reprinted from the *Journal of Polymer Research*, Vol. 1, No. 1, pages 1–13, January 1946. Preliminary reports of this work were presented at the Conference on Rubberlike Elasticity at the Polytechnic Institute of Brooklyn, April 3, 1943, at the meeting of the Society of Rheology in New York, October 30, 1943, and at the Symposium on the Theory of Long-Range Elasticity, at the Cleveland meeting of the American Chemical Society, April 4, 1944.

certain rubber samples, confirming the assumption that entropy changes, rather than energy changes, are primarily responsible for rubberlike elasticity. Deviations from simple proportionality may reasonably be attributed, for the most part, to the additional effect of energy changes.

On the other hand, the deduced inverse proportionality between elastic modulus and molecular weight appears to be in definite disagreement with experiment. Provided the molecules are not too short, the molecular weight (or average chain length) seems to be unimportant. This is reasonable, for one would not expect a rearrangement of a portion of a long-chain molecule to be affected in any way by the length of the chain, provided neither of the chain ends is close.

Partly because of this difficulty and partly because it is believed that in vulcanized rubber and in many or most other samples of rubberlike materials the structure resembles more closely a giant network molecule (or an aggregate of a relatively small number of such molecules) than an assemblage of giant chain molecules, several attempts have been made to modify or extend the earlier treatments to make them apply to such a network structure. The most obvious, though not well-justified, way to modify the earlier results is to assume that the same equations hold, with the average chain length replaced by the average distance (measured along the chains) between cross-links, *i.e.*, between points where three chainlike sections of the molecule are joined together[3]. Attempts have also been made to deduce new formulas on the assumption of network models of special types[4], such as one in which points, distributed as are the atomic centers in a diamond crystal, are connected by flexible chains, four such chains extending from each "lattice point[5]," or on the assumption[6] that the average dimensions of a single molecule vary in the same way as the dimensions of the sample (if cubic when unstretched).

It is not the author's purpose to discuss these theoretical treatments here at this time. Instead, the problem will be tackled in a different manner. It will be assumed that long-range elastic extension is accompanied by a large number of internal processes—rearrangements of relative atomic positions—occurring without any breaking of C—C or other strong bonds. Certain relations between the macroscopically measurable quantities (stress, strain, temperature, etc.) and quantities (distance and energy changes, etc.) characteristic of the rearrangements will then be deduced. These results can later be correlated with structural models of various sorts.

Before entering into the mathematical development, the nature of these internal rearrangements may be briefly considered. As already implied, rubberlike elasticity can be related to the more or less easy rotation about the single bonds in long chains or chainlike segments of a network structure, stretching involving a change from a very random distribution of orientations about these bonds to a less random distribution.

Rotation about all single bonds does not occur with the same ease, and differences in elastic behavior of different materials are to some extent attributable to this fact. Theoretically and experimentally, it can be shown that a double bond in a chain facilitates rotation about neighboring single bonds. This is probably one reason for the great flexibility of the chains in ordinary rubber, in which every fourth bond in the chain is a double bond.

Internal rearrangements requiring a large number of atoms to move together at the same time do not readily occur, since too many other surrounding atoms must be pushed out of the way. For good, long-range elasticity, a substance should have a structure such that many easy rearrangements of small segments

of the chains are possible. To illustrate this, the structures of gutta-percha and rubber may be compared (Figure 2). In gutta-percha, the arrangement of chain bonds extending from each double bond is *trans;* in rubber, it is *cis.* A "swinging-door" type of rearrangement, involving motion, as a unit, of only

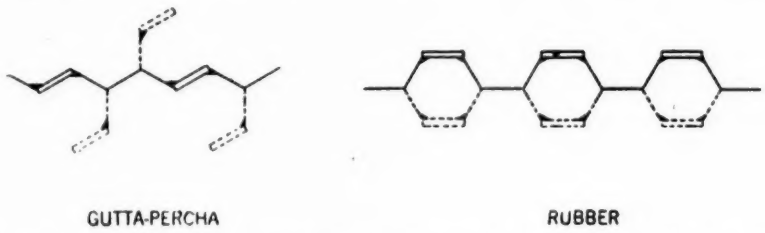


FIG. 2.—Representation of an important difference between the structures of gutta-percha and rubber.

two chain atoms (and the other nonchain atoms to which they are attached), can take place in rubber, but not in gutta-percha. Rotation about any of the single bonds in gutta-percha requires the simultaneous motion of many chain atoms, on the average—the exact number depending on the degree of straightness or kinkiness of the chain in the region concerned.

MATHEMATICAL TREATMENT

For simplicity, let us consider a hypothetical substance containing a large number of small rearrangeable systems, all exactly alike. For each such system we may draw an energy curve (Figure 3). Again for simplicity, let us assume

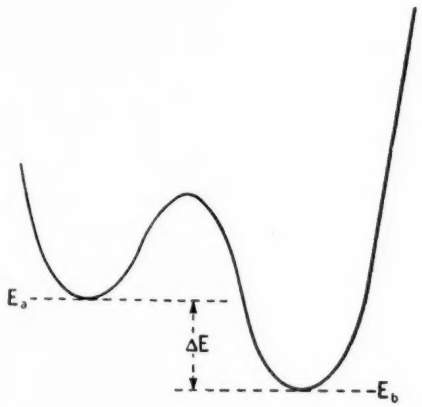


FIG. 3.—Energy curve for two orientations of a rearrangeable system.

only two minima in this curve, representing two energetically stable orientations of the system. There will be an energy hump between these two minima. How frequently it is passed over depends on the average kinetic energy of the atoms in the system (that is, on the temperature) and on the presence or absence of an external force tending to assist rearrangement. If the hindering hump is too high, the substance does not have rubberlike properties.

If this hump is sufficiently low, the different systems in the substance is distributed between the two possible orientations in such a way that more are in the orientation of lower energy—greater stability—at any given instant, provided no external force is applied. The application of an external force produces a shift in the relative numbers of systems in the two stages, increasing the number in the state which gives the greater extension in the direction in which the force is acting.

This simplified model can be readily treated by well-tested methods of statistical mechanics and thermodynamics. The probability that a system is in one of the two possible states is related to the energy difference between the two states in the absence of an external force, to the energy difference produced by the external force, and to the absolute temperature according to the equations:

$$P_a = \frac{1}{1 + \exp(\epsilon)} \tag{1}$$

and

$$P_b = \frac{\exp(\epsilon)}{1 + \exp(\epsilon)} \tag{2}$$

where

$$\epsilon = \frac{E_a - E_b}{kT} \tag{3}$$

Here, k is the Maxwell-Boltzmann constant and T is the absolute temperature.

The probabilities of the two states change as the energy difference between them changes (and so as the rubber is stretched), as shown in the curves of Figure 4, for the special case of zero initial energy difference.

The elastic modulus, G, is usually defined as the ratio of the stress, σ, to the strain, γ, the stress being the force, f, per unit initial cross-sectional area, A_0, of the sample, and the strain the increase in length, L, divided by the initial length, L_0. Denoting the volume of the sample, assumed to be independent of γ, by V:

$$\sigma \equiv \frac{f}{A_0} = \frac{fL_0}{V} \tag{4}$$

$$\gamma \equiv \frac{\gamma L}{L_0} \tag{5}$$

$$G \equiv \frac{\sigma}{\gamma} = \frac{fL_0}{V\gamma} \tag{6}$$

At constant pressure and volume, the force is related to the free energy change (ΔF) in the sample by the equation:

$$f = \frac{\mathrm{d}(\Delta F)}{\mathrm{d}(\Delta L)} = \frac{1}{L_0}\frac{\mathrm{d}(\Delta F)}{\mathrm{d}\gamma} \tag{7}$$

Therefore:

$$G = \frac{1}{V\gamma}\frac{\mathrm{d}(\Delta F)}{\mathrm{d}\gamma} \tag{8}$$

Our problem is to determine $\mathrm{d}(\Delta F)/\mathrm{d}\gamma$ as a function of γ, T, and quantities characteristic of the individual rearrangements occurring within the sample while it is being stretched.

Let us assume a hypothetical sample, cubic in shape before stretching, containing N independent, rearrangeable systems, all alike except that one-third are oriented so as to give, on rearrangement from state a to state b, an increase of the x coördinate of the moving atoms (but no change of any y or z coördinates), one-third are so oriented as to give changes in only y coördinates, and one-third so as to give changes in only z coördinates. We define p_x, p_y, and p_z as the probabilities that an x, y, or z system, respectively, is in the b state.

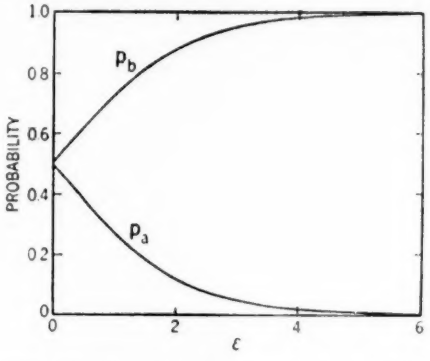


FIG. 4.—Dependence of the probabilities of two energy states of a rearrangeable system on the energy difference between them.

Model I.—We consider first a model substance in which, for each rearrangeable system, states a and b are of equal energy, in the absence of a stretching force. As a sample of this hypothetical substance is stretched—elongated in the z direction—the heat content, H, entropy, S, and free energy change in accord with the following equations:

$$\Delta H = 0 \tag{9}$$

$$\Delta S_x = \Delta S_y = -\frac{kN}{3} \ln \left[2p_x^{p_x}(1 - p_x)^{1-p_x}\right] \tag{10}$$

$$\Delta S_z = -\frac{kN}{3} \ln \left[2p_z^{p_z}(1 - p_z)^{1-p_z}\right] \tag{11}$$

$$\Delta F \equiv \Delta H - T\Delta S = -T(\Delta S_x + \Delta S_y + \Delta S_z) \tag{12}$$

Each x rearrangement causes a column of atoms, of cross-section a, and of length equal to the x distance between the rearranging system and the nearer end of the sample (average length = $L_x/4$), to shift a distance d_x in the x direction from the center of the sample. The average volume shift per rearrangement is thus $a_x L_x/4$. An infinitesimal change of the probability that an x system is in the b state, $\mathrm{d}p_x$, causes $N_x \mathrm{d}p_x$ systems to shift. The accompanying change in the length of the sample is $\mathrm{d}L_x$ and the average shift of each unit volume of the sample (in the x direction from the center) is $\mathrm{d}L_x/4$. Therefore:

$$\frac{V\mathrm{d}L_x}{4} = \frac{a_x L_x}{4} d_x N_x \mathrm{d}p_x \tag{13}$$

Similar equations hold for the y and z directions.

Assuming tentatively that a_x, a_y, and a_z are equal and independent of the

amount of stretch, and similarly with regard to d_x, d_y, and d_z, we introduce the abbreviations:

$$v \equiv a_x d_x \equiv a_y d_y \equiv a_z d_z \tag{14}$$

and

$$\nu \equiv \frac{N}{V} = \frac{3N_x}{V} = \frac{3N_y}{V} = \frac{3N_z}{V} \tag{15}$$

We then obtain:

$$\mathrm{d} \ln L_x = \frac{v\nu}{3} \mathrm{d}p_x \tag{16}$$

with similar equations in y and z. Integrating these equations leads to the relations:

$$p_x = \frac{3}{v\nu} \ln \left(\frac{L_x}{L_0} \right) + \frac{1}{2} \tag{17}$$

$$p_y = \frac{3}{v\nu} \ln \left(\frac{L_y}{L_0} \right) + \frac{1}{2} \tag{18}$$

and

$$p_z = \frac{3}{v\nu} \ln \left(\frac{L_z}{L_0} \right) + \frac{1}{2} = \frac{3}{v\nu} \ln (1 + \gamma) + \frac{1}{2} \tag{19}$$

Assuming incompressibility of the sample:

$$V \equiv L_x L_y L_z = L_x^2 L_z = L_y^2 L_z = \text{constant} \tag{20}$$

Making use of this relation, Equations (17) and (18) reduce to:

$$p_x = p_y = \frac{1}{2} - \frac{3}{2v\nu} \ln (1 + \gamma) \tag{21}$$

From Equations (4), (7), (10), (11), and (12) it is easily shown that:

$$\sigma = \frac{1}{V} \frac{\mathrm{d}(\Delta F)}{\mathrm{d}\gamma} = \frac{kT\nu}{3} \left[2 \ln \left(\frac{p_x}{1 - p_x} \right) \frac{\mathrm{d}p_x}{\mathrm{d}\gamma} + \ln \left(\frac{p_z}{1 - p_z} \right) \frac{\mathrm{d}p_z}{\mathrm{d}\gamma} \right] \tag{22}$$

Substitution of Equations (19) and (21) and their differentials with respect to γ leads to:

$$\sigma = \frac{kT}{v(1 + \gamma)} \ln \left\{ \frac{[1 + 2K \ln (1 + \gamma)][1 + K \ln (1 + \gamma)]}{[1 - 2K \ln (1 + \gamma)][1 - K \ln (1 + \gamma)]} \right\} \tag{23}$$

where

$$K = 3/v\nu \tag{24}$$

The initial elastic modulus, corresponding to this equation, is readily shown to be:

$$G_0 = \frac{18kT}{\nu v^2} \tag{25}$$

Stress-strain curves computed from Equation (23) are shown in Figure 5. The initial elastic modulus shows the expected proportionality with the absolute temperature, also an inverse proportionality with ν, the number of rearrangeable systems per unit volume, and with the square of the volume swept out by each rearrangement. These relationships seem reasonable. The curves show a falling off in elastic modulus, indicated by a decreasing slope of the stress-strain curve (Figure 5), with increasing strain, followed, at higher

strain values, by a sharp increase in stress (and in modulus). For this simplified model, the stress goes to infinity at:

$$\gamma = \exp\left(\frac{\nu\nu}{6}\right) - 1 \tag{26}$$

It is unnecessary to introduce additional assumptions, such as crystallization, to account for the upsweep of stress-strain curves at high strain values, although, if they occur, crystallization and related phenomena involving internal energy changes must modify the shapes of these curves.

In one important respect the stress-strain curves for this simple model are not in accord with experimental results. According to James and Guth[7], the minimum slopes of these curves, for experimental rubber samples, are usually about one-third of the initial slopes. Although this relationship holds, with our model, for a certain value of the product, $\nu\nu$, there is no apparent reason for

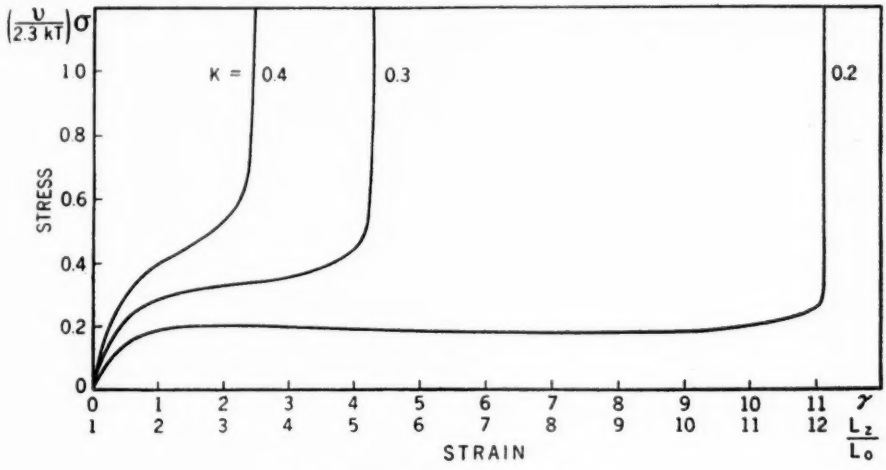


FIG. 5.—Stress-strain curves for Model I.

its general applicability. One may guess that the reason for this discrepancy lies in our tentative assumption that the N_x, N_y, N_z, a_0, and d_0 values are all independent of the strain or in the assumption that the rearranging systems can be treated as independent of one another.

A priori it is difficult to see just how our assumptions should be modified to bring them more into conformity with actual systems. We can, however, try various simple modifications, to see if any of them lead to the ratio of initial and intermediate slopes mentioned above. This has been done. We shall discuss here only one of these modifications, justifying our added assumption only by the fact that it leads to stress-strain curves very similar to those experimentally obtained.

Model II.—We assume constant values of N_x, N_y, N_z, and $a_x(= a_y = a_z)$, as in Model I, but assume d_x, d_y, and d_z to vary with extension of the sample according to Equations (27) and (28):

$$d_x = d_y = d_0(L_x/L_0)^2 \tag{27}$$

$$d_z = d_0(L_z/L_0)^2 \tag{28}$$

Substituting in Equation (13) and proceeding as before, we arrive at the relation:

$$\sigma = \frac{kT}{v}\left\langle \ln\left(\frac{1+K\gamma}{1-K\gamma}\right) + (1+\gamma)^{-3}\ln\left\{\frac{1+K[1-(1+\gamma)^{-2}]}{1-K[1-(1+\gamma)^{-2}]}\right\}\right\rangle \quad (29)$$

The initial modulus is again given by Equation (24). The stress becomes infinite when:

$$\gamma = \gamma_\infty = \frac{v\nu}{3} = \frac{1}{K} \quad (30)$$

Figure 6 shows stress-strain curves for three values of K. To show best the effect of changing K on the shape of the curve, σ/G_0 has been plotted, rather than σ. It is seen that these curves show minimum slopes which approximate one-third of the initial slopes. Comparison with experimental curves, such as that for a vulcanized rubber sample studied by Anthony, Caston, and Guth[8], which is reproduced as a dashed line in Figure 6, shows as good agreement as could be expected, considering the simplicity of the model assumed. (The ordinate scale for this experimental curve is to some extent arbitrary, because of the difficulty of determining accurately the initial slope from the published graph.)

Let us now consider the effect of an initial difference between the energies of the two states of each rearrangeable system.

Model III.—We assume everything as for Model II except that (in the unstretched sample) in half of the x (or y, or z) systems the energy of state b is higher than that of state a by an amount ΔE_0, and in the other half the energy of state b is lower than that of state a by the same amount.

For this model we obtain the following relationships, from which stress-strain curves can be computed:

$$\sigma = \frac{kT}{v}[\epsilon_z(1+\gamma)^{-3} - \epsilon_x] \quad (31)$$

$$\phi_x = \frac{1-\psi_x^2}{1+[\exp\epsilon_0 + \exp(-\epsilon_0)]\psi_x + \psi_x^2} \quad (32)$$

$$\phi_z = \frac{1-\psi_z^2}{1+[\exp\epsilon_0 + \exp(-\epsilon_0)]\psi_z + \psi_z^2} \quad (33)$$

Here ϵ_0, ϕ_x, ϕ_z, ψ_x, and ψ_z are abbreviations, defined by these equations:

$$\epsilon_0 \equiv \Delta E_0/kT \quad (34)$$

$$\phi_x \equiv -K\gamma \quad (35)$$

$$\phi_z \equiv K[1-(1+\gamma)^{-2}] \quad (36)$$

$$\psi_x \equiv \exp(-\epsilon_x) \quad (37)$$

$$\psi_z \equiv \exp(-\epsilon_z) \quad (38)$$

K, as before, is given by Equation (24).

The effect on the stress-strain curves of varying ϵ_0, with K constant, is

shown in Figure 7. The initial modulus for this model is given by the relation

$$G_0 = \frac{18kT}{\nu v^2}\left[\frac{2 + \exp \epsilon_0 + \exp(-\epsilon_0)}{4}\right]$$
$$= \frac{18kT}{\nu v^2}\left\{\frac{[1 + \exp \epsilon_0][1 + \exp(-\epsilon_0)]}{4}\right\} \tag{39}$$

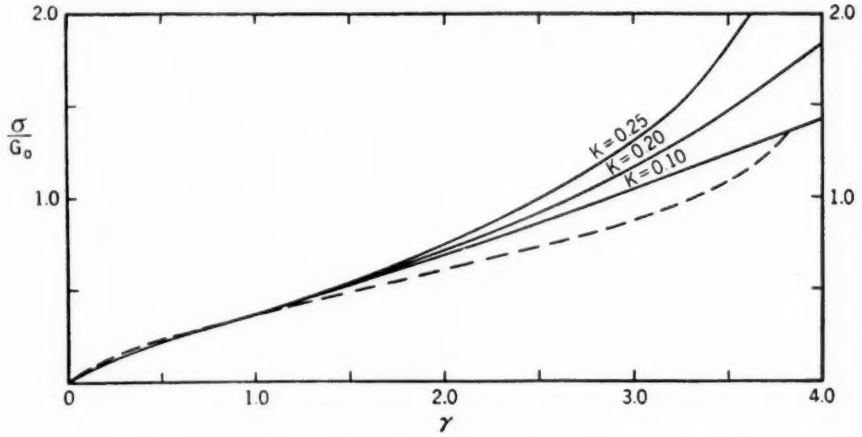


FIG. 6.—Stress-strain curve for Model II for different values of K. The dashed line is an experimental curve for a sample of vulcanized rubber.

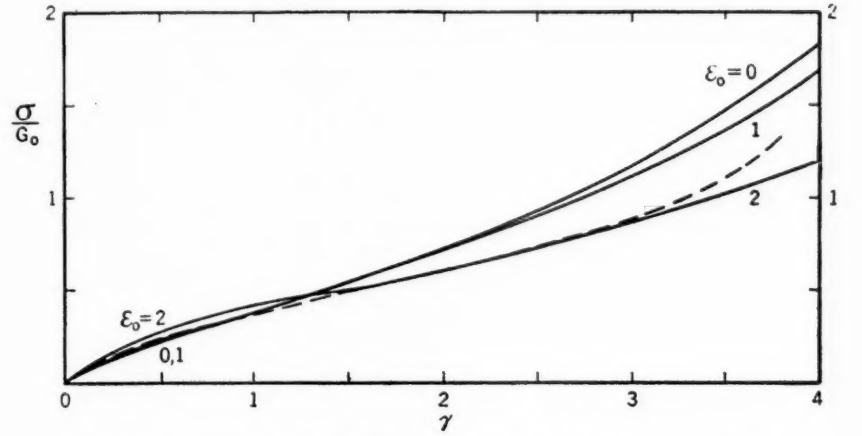


FIG. 7.—Stress-strain curves for Model III. The dashed line is an experimental curve[3].

Figures 8 and 9 show the dependence of the initial modulus on ϵ_0 and on T (for ΔE_0 constant), according to this equation. The limiting value of the strain, for infinite stress, is again given by Equation (30).

With this model the stress can be considered to be made up of an energy component and an entropy component

$$\sigma = \sigma_E + \sigma_S \tag{40}$$

The entropy component is given, according to thermodynamics by the relation:

$$\sigma_S = T\left(\frac{\partial \sigma}{\partial T}\right)_\gamma \tag{41}$$

Applying these to Equations (31) to (33), the following expression is obtained for σ_E:

$$\sigma_E = \frac{kT}{v}\epsilon_0[\exp(-\epsilon_0) - \exp\epsilon_0]\left\langle \frac{1-\psi_x^2}{(1+\gamma)^3\{[\exp\epsilon_0 + \exp(-\epsilon_0)](1+\psi_x^2)+4\psi_x\}} - \frac{1-\psi_x^2}{[\exp\epsilon_0+\exp(-\epsilon_0)](1+\psi_x^2)+4\psi_x}\right\rangle \tag{42}$$

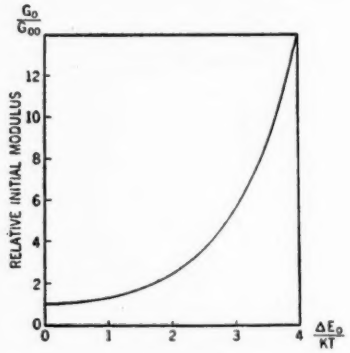


FIG. 8.—Dependence of initial elastic modulus on $\Delta E_0/kT$, for Model III, according to Equation (39).

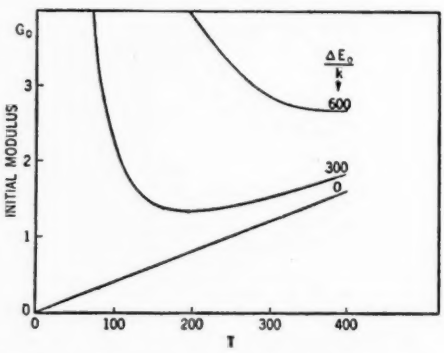
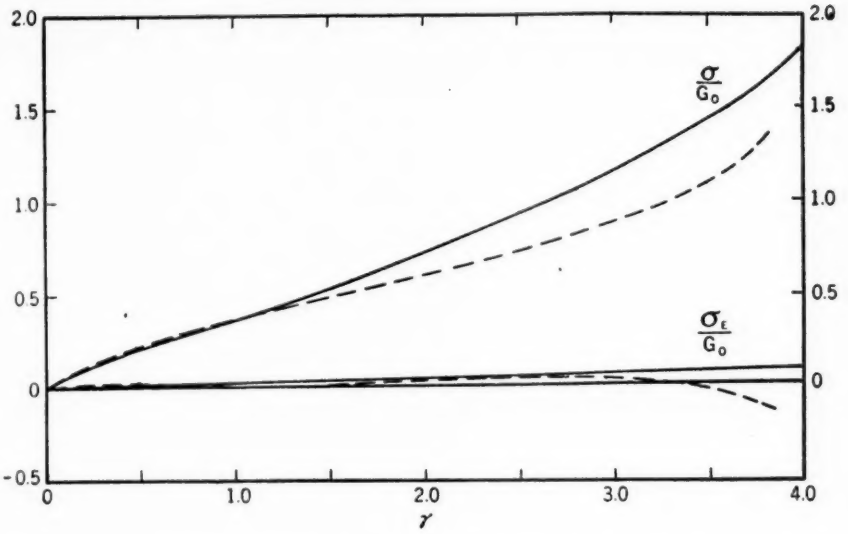
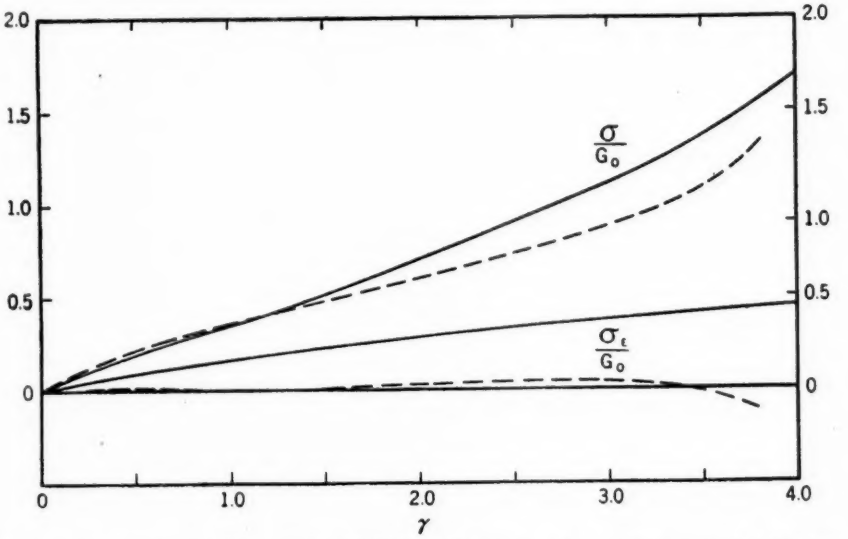


FIG. 9.—Dependence of initial elastic modulus on the absolute temperature, for certain values of $\Delta E_0/k$, for Model III, according to Equation (39).

Figures 10 and 11 show curves for σ and σ_E, each divided by the initial modulus, G_0, for certain values of K and ϵ_0. In an actual rubberlike material, initially containing rearrangeable systems with ϵ_0 different from zero, stretching would tend to orient these systems all in the same direction. At higher extensions, therefore, one would expect departures from stress-strain curves characteristic of Model III in the direction of those computed for a model in which all





FIGS. 10 AND 11.—Stress-strain curves for Model III, with curves for the energy component of the stress $K = 0.20$; $E_0 = 0.40$ (Fig. 10) and 1.00 (Fig. 11). The dashed lines represent experimental results.[10]

the systems of each type (x, y, z) are oriented in the direction favored by the stretching force. This model we shall call Model IV.

Model IV.—This is like Model III except that for all systems state b is initially lower in energy than state a by the amount ΔE_0. For this we obtain:

$$\sigma = \frac{kT}{v}\left\langle \ln\left(\frac{A + K\gamma}{B - K\gamma}\right) + (1+\gamma)^{-3}\ln\left\{\frac{A + K[1-(1+\gamma)^{-2}]}{B - K[1-(1+\gamma)^{-2}]}\right\} - \epsilon_0[1 + (1+\gamma)^{-3}]\right\rangle \quad (43)$$

where

$$A \equiv \frac{2}{1 + \exp(-\epsilon_0)} \tag{44}$$

$$B \equiv \frac{2}{1 + \exp \epsilon_0} \tag{45}$$

and K has the value given by Equation (24).

The initial slope is:

$$G_0 = \frac{kT}{v}\left[3K\left(\frac{A+B}{AB}\right) - 3\ln\left(\frac{A}{B}\right) - \epsilon\right] \tag{46}$$

The stress becomes infinite when:

$$\gamma = \gamma_\infty = B/K \tag{47}$$

The energy component of the stress is given by the equation:

$$\sigma_E = -\frac{kT\epsilon_0}{2v}[1 + (1+\gamma)^{-3}] \tag{48}$$

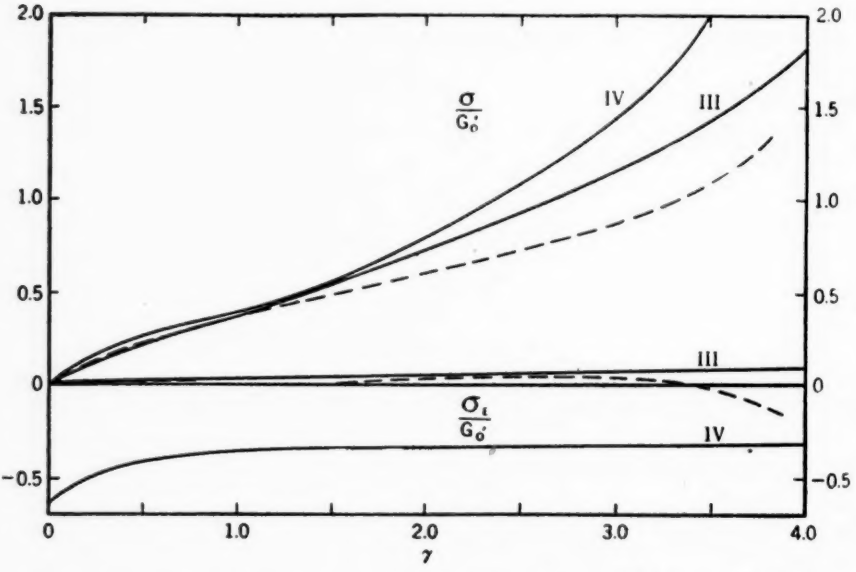


FIG. 12.—Comparison of stress-strain curves and their energy components for Models III and IV.

Figure 12 shows, for both Model III and Model IV, σ/G_0' and σ_E/G_0' curves for $K = 0.20$, $\epsilon_0 = 0.40$; G_0' is the initial modulus for Model III (Equation 39). The curves for an actual sample might be expected to approximate those for Model III at low elongations, deviating somewhat toward the Model IV curves as the elongation increases.

It may be noted that other factors not considered here—such as the lower energy (greater stability) of packing of the molecular chains when they are

elongated with parallel axes (with or without actual crystallization)—certainly affect the variation with elongation of the energy component of the stress, and so the total stress. In general, one would expect these factors to lower the actual stress-strain curves more and more as the elongation increases. In agreement with this, the experimental curves fall somewhat below those computed from the simple theory outlined here.

To see the effect of having a mixture of rearranging systems with different values of v, we consider Model V.

Model V.—We assume two types of systems with different values of v but otherwise the same. As for Model II, we assume no initial difference between the energies of the two states, a and b. Let:

$$\alpha \equiv v_1/\bar{v} \tag{49}$$

and

$$\beta \equiv v_2/\bar{v} \tag{50}$$

Using the definitions of Equations (35) to (38), and (24), with v replaced by $\bar{v}$, the average value, it can be shown that equation (31) holds, with this same substitution. The relationships between ϕ_x, ϕ_z, ψ_x, and ψ_z are as follows:

$$\phi_x = \frac{1 + (\alpha - 1)\psi_x^{\beta} + (\beta - 1)\psi_x^{\alpha} - \psi_x^2}{1 + \psi_x^{\alpha} + \psi_x^{\beta} + \psi_x^2} \tag{51}$$

$$\phi_z = \frac{1 + (\alpha - 1)\psi_z^{\beta} + (\beta - 1)\psi_z^{\alpha} - \psi_z^2}{1 + \psi_z^{\alpha} + \psi_z^{\beta} + \psi_z^2} \tag{52}$$

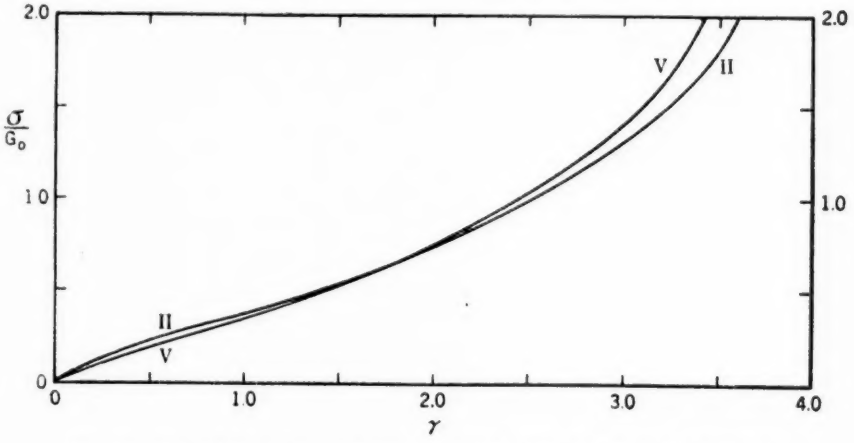


FIG. 13.—Comparison of stress-strain curves for Models II and V, illustrating the effect of a mixture of rearrangements having two different values of v.

A stress-strain curve calculated from these relationships is shown in Figure 13. This is for $K = 0.25$, $\alpha = 0.2$, and $\beta = 1.8$, corresponding to v_2 equal to $9v_1$.

The initial modulus is given by the equation:

$$G_0 = \frac{kTK}{\bar{v}}\left(\frac{48}{\alpha^2 + \beta^2 + 4\alpha + 4\beta - 6\alpha\beta + 4}\right) \tag{53}$$

The stress becomes infinite when:

$$\gamma = \gamma_\infty = \frac{\nu\bar{v}}{3} = \frac{1}{K} \tag{54}$$

It is seen that the shape of the curve differs, but not greatly, from that computed on the assumption that all v values are alike.

SUMMARY AND CONCLUSION

It has been shown that for a simple hypothetical model substance, containing like independent systems, each capable of existing in two alternative orientations, stress-strain curves may be computed which are similar in form to those ordinarily obtained from rubber and rubberlike materials, provided one introduces a certain dependence of the volume shift per rearrangement on the elongation. With this model, the dependence of the initial elastic modulus and that of the shape of the stress-strain curve on various characteristics of the rearranging systems are readily studied.

More detailed comparison of these theoretical results with experimental data and with other theoretical treatments will be postponed until a later date.

ACKNOWLEDGMENT

In conclusion, the author is pleased to acknowledge the competent help of (Mrs.) Dorothy O. Davis and (Mrs.) Ruth M. Welch with the calculations involved in the development of this theory and the preparation of this paper.

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MOLECULAR PROCESSES DURING DEFORMATION OF RUBBERLIKE ELASTIC BODIES *

KURT H. MEYER AND A. J. A. VAN DER WYK

CHEMISTRY LABORATORY OF THE UNIVERSITY, GENEVA, SWITZERLAND

INTRODUCTION

It has been demonstrated[1] that the elastic force of a moderately vulcanized rubber kept at a constant stress is proportional to the absolute temperature, T, in the region of medium elongations. In this respect, rubber behaves somewhat like an ideal gas, the pressure of which at constant volume is also proportional to T. By applying the first and second laws of thermodynamics, it can be shown that the internal energy of isothermally stretched rubber changes as little as that of an ideal gas if its volume is increased or decreased isothermally. In both cases, however, the entropy of the system changes.

Meyer, Susich, and Valkó[2], Karrer[3], and Busse[4] explain this behavior in the following way. All rubberlike substances consist of long, flexible, chain molecules whose links are thermally mobile. In the undeformed amorphous rubber, the molecules represent randomly coiled chains; as a result of the deformation their shape is changed, *e.g.*, partly stretched by elongation. Thus a thermodynamically less probable shape is forced on them; the thermal agitation tends to eliminate it; because of the reciprocal felting and intertwining of the molecules, a return to the thermodynamically more probable state is possible only if the deformation can be reversed.

The thermally mobile chain links are referred to as kinetic units or chain segments.

In the present paper, we shall discuss the molecular processes taking place in the course of deformation, in particular such questions as: "How is the deforming force transferred to an individual chain molecule and its segment?" "How does the molecule react to this force?" After having discussed these questions, we shall examine how far the requirements are complied with for a quantitative theory such as the derivation of an equation to calculate the modulus of elasticity from structural data. We shall also discuss the attempts known to have been made in this direction so far.

STATE OF AGGREGATION OF RUBBER (RUBBERLIKE STATE)

To be able to understand the molecular processes which take place during deformation, we must first of all attempt to form as exact a picture as possible of the state of aggregation and the fine structure of undeformed rubber. Since complete crystallization removes the rubbery behavior, a fine structure corresponding to a rigid latticelike framework is out of the question. Rubberlike elasticity is closely connected with a highly disordered and amorphous state. Rubber and similar substances differ from ordinary amorphous substances, such as silica glass, in that they can easily be deformed reversibly to a high

* Reprinted from the *Journal of Polymer Research*, Vol. 1, No. 1, pages 49–57, January 1946.

extent; relatively small deformations are instantaneously reversible, but the internal friction of rubber is so large that in practice it always retards the retraction slightly. It is possible to measure the friction occurring during such deformation by the damping of slow oscillations[5]. The limiting value of the viscosity at disappearing deformation and speed of deformation is a constant for a particular substance. For unvulcanized and slightly vulcanized rubber, it has a magnitude of 10^6 c.g.s. units at 20° C, and rises to about 10^7 c.g.s. at temperatures slightly below 0° C. If the temperature is lowered further, the viscosity exceeds 10^8 c.g.s. units and the typical rubber elasticity begins to disappear. At still lower temperatures, the rubber becomes a brittle, glasslike solid. The transition from the elastic to the brittle state is thus accompanied by an increase of viscosity like the one taking place during the transition of a viscous liquid to a glasslike solid.

For rubberlike elasticity to occur, it seems necessary that the individual segments of the long-chain molecules possess a considerable mobility, so that the segments of adjacent chains can freely slide over each other and change their relative positions, just as the molecules in a liquid do. In this respect, a rubberlike elastic material exhibits the properties of a viscous fluid. However, while in a liquid each single molecule is connected with all its neighbors by relatively weak intermolecular forces, each segment of a long-chain molecule in rubber is tied to two or more of its neighbors by strong chemical bonds, forming fiber molecules which are intertwined and entangled. If these fiber molecules are sufficiently long, it becomes very improbable that two entire chains slide over each other as a whole, and hence the overall shape of the relaxed sample is maintained. The safest way to protect the entangled mass of randomly coiled chains against permanent deformation is by interspersed strong cross-links, which knit all individual molecules together into one big, wide-meshed, net molecule.

In the following discussion, we must therefore keep in mind that, as far as the mobility of the segments and the local convolutions of the chain molecules are concerned, rubbers show the peculiar properties of a liquid, whereas the overall behavior of a macroscopic piece of rubber has the characteristics of an elastic solid, because of the system of strong cross-bonds which it contains.

MOLECULAR PROCESSES DURING DEFORMATION OF A VISCOUS LIQUID

In a liquid or an amorphous glasslike solid, the molecules are not distributed in a completely irregular way, as in a gas; under the influence of the intermolecular forces, they take up positions which are determined by certain minimum distances from their next neighbors. If one deforms a viscous fluid or an amorphous solid, the stress or shear is transferred to all molecules by equal intermolecular forces[6]; they are slightly removed from their equilibrium positions during the deformation, so a tension arises. The molecules try to avoid this state of stress by sliding over each other to occupy new positions, in which the mean distances between nearest neighbors and the geometrical arrangement of the molecules are again the same as previously. The decay of tension can be observed experimentally if one forces a finite deformation on an amorphous viscous fluid and measures the stress relaxation. The simplest behavior would be an exponential stress decay, but, in reality, the decay of the tension, *e.g.*, in deformed pitch, is of a far more complicated character[7]. In the state of equilibrium of an amorphous material, not only the position but also the orientation of its molecules, the shape of which strongly deviates from

the spherical, is influenced by their nearest neighbors. As a consequence of deformation, the reciprocal orientation between the molecules is disturbed, and during relaxation the original state is restored. Besides, the configuration of flexible macromolecules is being affected by a deforming force, and the return of the distorted molecules to the original shape represents another contribution to the process of relaxation.

Let us now consider the distance between two individual molecules which are far apart; for example, in a softening glass during deformation. Depending on the type of deformation and their relative position, the molecules become farther removed from each other or are brought closer together. During the rearrangement caused by an extension, the distances are, on the average, increased, calculable in the following simple way.

Let us suppose that a molecule, 1, in the unstretched sample lies at a distance, D_0, and in the direction, θ_0, from any other molecule, 0. Through the latter we place a rectangular system of coördinates, whose z axis runs parallel

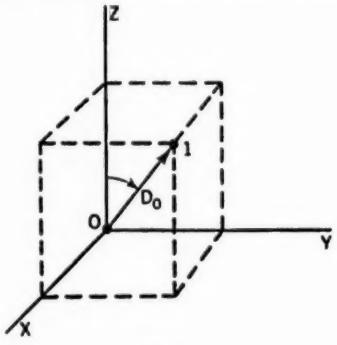

FIG. 1

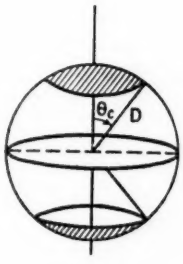

FIG. 2

to the direction of the stretch (see Figure 1). The original distance between the two molecules is given by:

$$D_0^2 = x^2 + y^2 + z^2 \tag{1}$$

Now let us stretch the sample by a factor, λ, in the z direction. The distance between the two molecules now becomes:

$$D_\lambda^2 = x^2/\lambda + y^2/\lambda + z^2\lambda^2 \tag{2}$$

Therefore:

$$D_\lambda^2 - D_0^2 = (D_\lambda - D_0)(D_\lambda + D_0) = (x^2 + y^2)(1/\lambda - 1) + z^2(\lambda^2 - 1) \tag{3}$$

It is thus possible to choose molecule No. 1 in such a way that the distance between the two molecules remains unchanged during the stretching, *i.e.*, that $D_\lambda - D_0$ equals zero. Let us call these coördinates x_c, y_c, and z_c. Then obviously:

$$(x_c^2 + y_c^2)(1 - 1/\lambda) = z_c^2(\lambda^2 - 1) \tag{4}$$

or, since:

$$\frac{x^2 + y^2}{z^2} = \tan^2 \theta_c \tag{5}$$

$$\tan^2 \theta_c = \lambda(\lambda + 1) \tag{6}$$

All molecules at a distance D_0 from molecule zero, whose distance from the latter is increased by stretching ($D_\lambda > D_0$) are positioned on a spherical surface with an angular aperture of $2\theta_c$ (see Figure 2). In the unstretched sample, an equal number of molecules lie in every direction at a given distance from molecule zero, provided that this distance is not chosen too small. The number of molecules lying on a cone having the z direction as axis and the angular aperture, θ_c, divided by the total number of molecules is equal to the surface of the calotte divided by surface of the hemisphere. This ratio, α, is then given by:

$$\alpha = (1 - \cos \theta_c) \tag{7}$$

Thus, α denotes that fraction of the molecules which are moved away from the molecule zero during extension. Relations (6) and (7) hold for all molecules not lying on the surface of the sample and not too close to the molecule zero. The data in Table I were calculated with Equations (6) and (7).

TABLE 1

VALUES OF θ_c AND α AS A FUNCTION OF ELONGATION

λ	0.5	0.9	1.0	1.1	1.303	2.0	4.0	7.0
θ_c	40.9°	52.6°	54.7°	56.6°	60°	67.8°	77.4°	82.4°
α	0.244	0.393	0.422	0.450	0.500	0.622	0.782	0.868

It can be seen that at extensions above 30.3 per cent ($\lambda > 1.303$), more than 50 per cent of all molecules increase their distance from any molecule chosen at random. These distances are always increased for the majority during buckling ($\lambda > 1$).

BEHAVIOR OF SEGMENTS DURING DEFORMATION OF RUBBER

These observations must now be referred to a rubberlike elastic substance. Under the influence of a deforming force, all segments are taken out of their equilibrium positions and probably also deformed, so a force arises which is opposed to the tension; the segments evade the force by sliding over each other, so the tension is relaxed. In a liquid, any molecule can exchange place equally easily with all its neighbors; but in a rubberlike high polymeric substance a segment cannot change places with two of its neighbors, *i.e.*, the neighbors forming adjacent parts of the same chain. By means of these neighbors the segments are linked together to fibers, which in turn are felted together into the bulk material. The intramolecular arrangement thus remains different from the original arrangement in the undeformed state, even after the segments have taken up their new positions and shapes. The elastic tension characteristic for rubber remains: the relaxation is limited.

Let us now look at the fate of any chain molecule during stretching of the substance by observing the change of position of several segments which are far away from each other. They behave like the molecules of a viscous liquid: some approach each other, but the majority draw farther apart. Therefore, the long-chain molecules are stretched over certain regions in such a way that bends disappear, but all the molecules become arranged in folds parallel to the direction of stretching. This can best be seen from a schematic figure (Figure 3).

Provided the chains are sufficiently long to preserve the felt texture, this enforced arrangement of them is independent of the length of the chain mole-

cules at small and medium deformations. In the same way a small percentage of inserted cross-linkages has either no influence at all or only a very minute one.

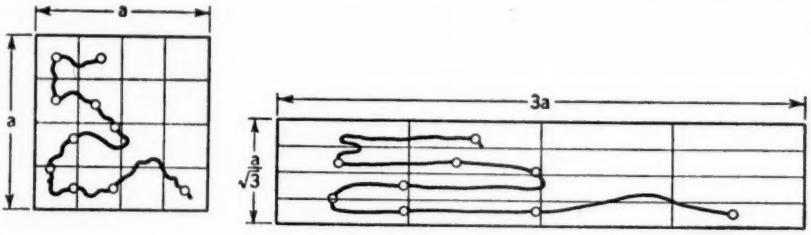

FIG. 3

EXPERIMENTAL RESULTS

The qualitative theory of the molecular processes during deformation, as stated here, does not contradict any experimental fact, and explains certain phenomena to which only little attention has been paid thus far. The stress relaxation can be ascertained by comparing the socalled "dynamic modulus" computed from the tension measured during the deformation with the "static modulus". According to Kosten[8], the dynamic modulus is 2.4×10^7 dynes per cm.^{2} after 1/40 second, while the static modulus is about 1×10^7.

Furthermore, the following results, which may be tested experimentally, can be deduced: Since the rearrangement during deformation depends solely on the type and amount of deformation, the elastic force for the same deformation must be the same, or at least of the same order of magnitude, for different substances consisting of chain molecules which have a similar flexibility, *e.g.*, they must show a similar elastic modulus of stretching. Further, the force must be independent of the molecular weight, as long as this is sufficiently large to prevent irreversible slipping and thus a permanent set. As cross-linkages cannot exert any influence on the rearrangement, vulcanization with a small amount of sulfur does not influence this force either. If, however, the flexibility is seriously restricted by too many cross-linkages or by embedded fillers, the equality can no longer be expected.

As a test we have recently determined or tabulated the moduli of elasticity of a number of rubberlike elastic substances.

The elastic modulus of stretching referred to the actual cross-sectional area depends on the degree of stretching; according to Weise[9] it shows a flat minimum at an extension of 70 per cent, then rises, slowly at first, and more rapidly above 800 per cent. Up to an extension of 50 per cent, however, the modulus varies only between 1.1 and 0.9×10^7 dynes per cm.^{2} It therefore seems advisable to compare mean values of elongation, like those which can be read from stress-strain curves already published or which can be obtained experimentally. If, for instance, the force, F, is measured at an extension of 10 to 30 per cent and referred to the cross-sectional area, s, of the stretched piece. The modulus, E, then is given by:

$$E = (F/s)/(\Delta l/l_0)$$

where l = elongation and l_0 = original length.

In our own experiments, standard pieces were stamped out of thin sheets and stretched by means of attached weights; the extension was measured

cathetometrically immediately afterward. For all substances, except for masticated rubber, the elongation remained practically constant after a few seconds. Sulfur threads of a diameter of 0.5 mm. were obtained by pouring heated sulfur into water; these were examined immediately after having been made. Further flow occurred after a specific elongation for degraded rubber. A specific length was therefore read off after the weights were put on, and the load was removed at the moment of taking the reading so that a contraction took place; Δl was based on this contraction.

Of the materials listed in Table II, the following can be regarded as linear

TABLE II

ELASTIC MODULUS OF VARIOUS POLYMERIC MATERIALS

Material	$\Delta l/l_0$	F/s (g. per sq. cm.)	E (dyne per sq. cm. $\times 10^7$)
Film of hevea latex[10]	0.25	30	1.2
Slightly vulcanized rubber[9]	0.1	10	1.0
Slightly vulcanized rubber[11]	0.11	13	1.2
Somewhat more highly vulcanized rubber, 7% sulfur of which 3% is bound sulfur[11]	0.5	53	1.1
Neoprene, vulcanized, 10% magnesium oxide[12]	1.0	240	2.4
GR-S, butadiene-styrene copolymer, 2% sulfur[13]	0.1	12	1.2
Elastic sulfur[14]			0.6
Polyphosphonitrile chloride[15]	0.5	100	2.0
New Experimental Results			
Slightly degraded rubber (*feuille anglaise*)	0.16	11	0.7
Buna (butadiene-sodium polymer), 7% sulfur of	0.093	11	1.2
which 3% is thio sulfur	0.14	17	1.2
Perbunan (butadiene-acrylonitrile copolymer)	0.054	13	2.4
vulcanized	0.11	25	2.4
Polyisobutylene (unvulcanized)	0.09	6	0.7
	0.18	15	0.8
Elastic sulfur	0.19	12	0.6
Elastic fiber from animal tissue (ox ligament)	0.10	13	1.3

polymers without any cross-linkages; native rubber, sulfur, and polyphosphonitrile chloride. The molecular weight of the native, undegraded rubber can be estimated at 400,000 to 500,000; that of the examined sample of *feuille anglaise* (slightly degraded rubber) has been determined osmotically as 130,000, and that of the polyisobutylene as about 250,000.

The molecular weight of elastic sulfur is probably very high. According to Rotinjanz[16], the viscosity of molten polymeric sulfur drops to one-tenth on adding no more than 0.02 per cent iodine, *i.e.*, one molecule of iodine per 40,000 atoms of sulfur. It can be deduced from this decrease in viscosity that each chain has been split into several fragments and that the original chains must therefore have contained a multiple of 40,000, but at least the double amount of sulfur atoms, corresponding to a molecular weight of 2,500,000.

When dealing with cross-linked polymers, such as vulcanized rubber or Buna, the entire sample may be regarded as a giant, three-dimensional molecule which does not have a molecular weight in the normal sense of the word. Because several authors have attributed a special importance to the average length of the parts of the chain lying between two cross-links, we have added these data in Table III. It can be estimated from the content of combined sulfur. The frequency of the thioether linkages can be determined by the methyl iodide method.

Table III contains the moduli of elasticity, E, and the molecular weights,

TABLE III

COMPARISON OF THE ELASTIC MODULUS AND MOLECULAR WEIGHT OF VARIOUS POLYMERIC MATERIALS

Material	Mol. wt.	E (dyne per sq. cm. $\times 10^7$)
A. Chain polymers (without cross-linkages)		
Slightly degraded rubber	130,000	0.7
Rubber made from latex (not vulcanized)	400,000	1.2
Polyisobutylene	250,000	0.8
Polyphosphonitrile chloride		2.0
Elastic sulfur	2,500,000	0.6

B. Net polymers (with cross-linkages)

Material	M^*	E
Slightly vulcanized rubber, 3% sulfur of which 1.5% is bound	2,000	1.2
More highly vulcanized rubber, 7% sulfur of which 3% is bound	1,000	1.2
Buna 85, vulcanized with 7% sulfur of which 3% is bound	1,000	1.2
Polychloroprene, vulcanized, 10% magnesium oxide		2.0
GR-S, 2% sulfur	2,000	1.2
Elastic fiber from animal tissue (cattle ligament)	..	1.3

M, of various linear rubbery polymers. M^* denotes the average weight of a chain fragment between two cross-links. It can be seen from Table III that there is little relation between the modulus of elasticity and the chemical constitution, in particular, the molecular weight or M^*.

LIMIT OF DEFORMATION

Since the density of amorphous rubber is only slightly smaller than that of crystalline rubber, the chain molecules must be very closely intertwined in the unstretched state. The molecular texture thus must be similar to that of a felt or of compressed cotton wool. If such a material is stretched, some of its fibers are adjusted parallel to the direction of stretching, and other parts are arranged in folds or snarls that can only be straightened out by applying a stronger force, which may possibly cause rupture.

There is no reason to suppose that the processes during the deformation of the rubber "felt" are of a fundamentally different nature. The modulus of elasticity of most rubbery substances rises steeply after 600 to 800 per cent extension. When stretching very slowly, it is possible to extend the sample a little farther; when stretching rapidly, the sample breaks. If linear chain polymers which have been stretched up to the breaking point crystallize, the parts of the chains within the crystallites are arranged parallel to the direction of stretch. It can, therefore, be presumed that a similar arrangement already exists in the highly extended amorphous state. If a piece of bulk rubber is stretched 700 per cent, a volume element of cubic shape is extended into a parallelopiped with an axis ratio of about 20. This very elongated rubber filament contracts again into a volume of the shape of a cube as soon as the stress is relaxed. Interpreted in molecular terms, this would mean that a straight-chain fragment consisting of 25 isoprene units (length 100 Å., width about 5 Å.) would form an approximately isodiametric structure after contracting.

QUANTITATIVE RELATIONS

Several authors have attempted to apply statistical mechanics to the problem of the deformation of an ideal rubberlike elastic substance. Most of the papers are based on an assumption which, in our opinion, does not completely correspond to the actual processes: the deforming force is supposed to attack only at certain definite points of the chain molecules. For linear polymers the ends of the chain molecules are supposed to be mainly attacked, and for net polymers the cross-links connecting two or more chains. Furthermore, it is usually presumed, either plainly or by implication, that the chain molecules in the rubber phase behave similarly to molecules of an ideal gas. This assumption is, of course, an oversimplification, because it is known from investigation of the thermodynamics of polymer solutions that the number of possible configurations of a rubber molecule in an athermal solution, *e.g.*, in toluene, is much larger than that in the amorphous state[17]. It seems, therefore, reasonable to assume that this number is also much larger in the gaseous state than in bulk rubber. The gaseous state cannot, therefore, quantitatively be taken as a basis for calculations for the rubberlike state.

Using the two hypotheses mentioned, several authors have computed the modulus of elasticity of rubbery polymers. Depending on the special assumptions made, the expressions obtained differ somewhat from each other. Table IV contains a number of expressions for the modulus of elasticity, E, in terms

TABLE IV

DERIVED EXPRESSIONS FOR THE ELASTIC MODULUS

Author	Year	Expression for modulus	Remarks
W. Kuhn[18]	1936	$7RT\rho/M$	Linear polymers without cross-linkages.
W. Kuhn[19]	1938	$7RT\rho/M^*$	Netted chain polymers (with cross-linkages).
H. Pelzer[20]	1938	$\frac{FkT\sqrt{2}}{b(M^*/m)^{7/6}}\left(fN\frac{\rho}{m}\right)^{2/3}$	F = fraction of number of chains per sq. cm. acting along direction in which stretch is applied; k = Boltzmann constant; b = length; m = molecular weight; f = number of freely rotating linkages of monomer unit.
E. Guth[21]	1941	$\frac{3qkT}{(M^*/m)b\cos\frac{\theta}{2}}[1+2(l_0/l)^3]$	q = number of chains per sq. cm. perpendicular to direction of stretching; k = Boltzmann constant; m = mol. wt. of monomer unit; b = length of monomer unit; θ = valence angle (C—C—C) = 109°36′; l/l_0 = relative extension.
F. H. Müller[22]	1941	$\frac{3}{5c}nkT\left(\frac{m}{M^*}\right)^{1/2}$	Netted chain polymers (with cross-linkages). c = numerical factor about 1; n = Avogadro number per cc.; k = Boltzmann constant; m = mol. wt. of monomer unit.
F. T. Wall[23]	1942	$F=\frac{RT}{M^*}\rho\left(\frac{l}{l_0}-\frac{l_0^2}{l^2}\right)$	F = restoring force of a cylindrical prism extended from l_0 to l and of cross-sectional area 1 sq. cm.
W. Kuhn[24]	1945	$\frac{24RT\rho}{5M^*}$	Netted chain polymers.

of the molecular weight, M, the weight of the chain fragment lying between two points of linkage, M^*, the density, ρ, the absolute temperature, T, and the gas constant, R.

It can be seen that, according to these equations, E depends on M or M^*. This, however, is not in agreement with the experimental facts as presented in Table II.

In our opinion any quantitative theory of rubber elasticity should follow a fundamentally different line. The theory of the liquid state ought to serve as a starting point for advances to the more complicated sphere of the rubberlike state. Since, however, until now there has been no satisfactory quantitative theory even for simple liquids, we must for the time being content ourselves with the qualitative considerations advanced here.

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STRUCTURAL CHANGES IN VULCANIZATION OF BUNA-S *

MAX H. KECK AND LAVERNE E. CHEYNEY

THE GOODYEAR TIRE AND RUBBER COMPANY, INC., AKRON, OHIO

The development and production on a commercial scale of synthetic rubber-like materials, particularly the butadiene copolymers, during the wartime emergency focused attention on phenomena associated with their vulcanization. These copolymers, particularly the synthetic tire copolymer known as Buna-S (GR-S in the United States), lend themselves to vulcanization with sulfur and the same types of accelerators used with natural rubber; the vulcanizates possess many points of similarity to those derived from the natural elastomer.

The literature on the vulcanization of natural rubber is quite extensive. Several reviews are available[1], although most of these are not entirely up to date. Among the more recent publications of direct interest in this connection are those of Farmer and coworkers[2] and of Armstrong, Little, and Doak[3].

The government general-purpose rubber known as GR-S is a copolymer of 3 parts by weight of butadiene and 1 part of styrene.[4] The polymerization is carried out in aqueous emulsion, and the final polymer may contain (1) unreacted monomer, which is usually well removed by "stripping", (2) low-molecular-weight polymers, (3) catalyst or its degradation products, (4) residual emulsifier or its conversion products, *e.g.*, soap and/or fat acids, (5) coagulants or their reaction products, (6) buffers, (7) auxiliary materials usually termed "modifiers", which influence the degree of cross-linking or branch-chaining in the polymer, (8) stopping agents for the polymerization, (9) anti-oxidants, such as phenyl-β-naphthylamine, which are added to prevent further polymerization in storage or transit. Thus, the so-called hydrocarbon polymer is not entirely pure hydrocarbon, and many of the variations in quality of the commercial product have been due in no small part to variations in number and quantity of these "nonrubber" impurities.

The concentrated research carried out on Buna-S to date has produced a considerable body of information, even though many of the data have not been published for reasons of national security. Buna-S possesses certain points of similarity to and certain differences from the natural polymer:

1. It is possible for polymerization to occur in the 1,2- as well as in the 1,4-position; branched chains and "pendant" vinyl groups result, and this would be expected to affect chemical behavior as well as physical characteristics[5]. Another contributing fact is the probability that both *cis* and *trans* structures exist in the same synthetic polymer. The natural polymer is believed to exist entirely in the *cis* modification.

2. Mathematical considerations and certain evidence[6] indicate styrene units to be randomly distributed throughout the chains. This, together with

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 37, No. 11, pages 1084–1089, November 1945.

the presence of branched chains produced by 1,2-polymerization, leads to a high degree of nonsymmetry in the polymer; it probably accounts for the fact that this polymer, unlike natural rubber, does not crystallize on stretching and the probably related fact that pure gum stocks have relatively poor strength. Kemp and Straitiff[7] believe that this lack of structural symmetry may be responsible for inability to cross-link and form a desirable structure in the vulcanizate.

3. The molecular weight is, in general, lower than that of natural rubber[8], and its distribution is quite broad[7]. It has been indicated[7] that the presence of the lowest molecular-weight polymers is detrimental to the quality of the vulcanizates. High-molecular-weight fractions, which compare favorably with natural rubber on the basis of molecular weight, tensile strength and modulus, are tough and hard to handle on a mill. This difference may be due to the activating influence of the side-chain methyl group in the natural polymer on reaction with oxygen and resultant degradation during milling. This activating effect has been noted in a number of other instances—*e.g.*, reactions with halogens, hydrogen halides, isomerizing agents, etc. It is well known that oxidative degradation accompanies the plasticization of natural rubber by milling[9].

4. Extension of the curing period of natural rubber stocks beyond the so-called optimum results in the phenomenon known as reversion. It is possible in certain cases to minimize this by the proper choice of accelerators[10]. Such reversion does not occur with Buna-S; instead, this polymer becomes progressively stiffer as cure progresses. It is worth noting that Hauser and Brown[11] believe the phenomenon of reversion to be associated with the action of oxygen. If this is true, the difference between the two types of polymers is probably associated with the type of activating effect noted above.

5. Hysteresis properties of the two types of vulcanizates are markedly different. The detrimental effect of heat build-up on the physical properties of the synthetic vulcanizates has been highly publicized. However, it should be noted that the action of heat alone (in the presence of air) is to cause further polymerization of the synthetic elastomer whereas, in the case of the natural polymer, heating in the presence of air causes oxidative degradation. Thus the difference in the action of heat may be oxidative in character and be associated with the activating influence of the methyl group in the isoprene unit.

UNSATURATION OF NATURAL RUBBER VULCANIZATES

Several investigators have attempted to measure the chemical unsaturation of natural rubber[12]. Of the various methods proposed, the iodine chloride titration method of Kemp[13] has proved most valuable. It was modified by Blake and Bruce[14] for the analysis of vulcanized stocks. Brown and Hauser[15] reported extensive work and certain generalizations utilizing this method with various rubber stocks.

In the case of rubber-sulfur vulcanizates, the loss of one double bond was found to accompany the combination of one atom of sulfur, whereas in accelerated stocks the combination was in a definite ratio of atoms of sulfur combined to number of double bonds lost during the early part of the cure, and in excess of the one-atom/double-bond ratio. After combination of most of the sulfur, additional loss of double bonds was due apparently to polymerization by heat under the influence of accelerators or some similar effect due to oxygen.

Explanation of the evident combination of sulfur in excess of one atom per

double bond saturated was explained by these authors in terms of several possible reactions: (1) addition, (2) bridging, (3) dehydrogenation, (4) polymerization. The first two types of reaction would produce a ratio of one atom of sulfur per double bond lost, as found in the simple rubber-sulfur compound. Reaction (1) is not in accord with observed properties of solubility, etc. If the ratio is greater than 1, an additional reaction must be taking place where sulfur can combine without loss of double bonds. Such a possibility might be reaction (3). Excess loss of unsaturation may be a polymerization reaction (4) after most of the sulfur has combined.

Recent work of Farmer and Michael[2] led them to believe that the primary reaction of vulcanization is a substitution reaction on the alpha carbon atom. This corresponds somewhat to the dehydrogenation reaction suggested by Brown and Hauser, but with the cross-linkage taking place at the carbon atom alpha to the double bond rather than on the doubly bonded one.

More positive evidence of sulfur substitution on the alpha carbon was presented recently by Armstrong, Little, and Doak,[3] who studied the reactions with vulcanizing agents of certain olefins which have structures similar to rubber. The chief products of reaction of these simple aliphatic monoölefins with sulfur zinc oxide, and soluble zinc soap in the presence of accelerators consisted of the olefin bridged by sulfur at the alpha carbon atom. It was also observed that the degree of cross-linking of rubber vulcanizates is closely related to the amount of zinc sulfide formed during the reaction, which is evidence in favor of a dehydrogenation type of reaction.

Selker and Kemp[16] recently presented evidence indicating that part of the combined sulfur in soft vulcanized natural rubber was attached to the alpha carbon atom.

EXPERIMENTAL PROCEDURE

Four related Buna-S stocks were employed for this study. They were selected from the group studied by Cheyney and Duncan[17] in determining the temperature coeficient of the Buna-S vulcanization reaction. They represented pure-gum and channel-black reinforced stocks, respectively, containing in each case 1 and 5 per cent added sulfur. Cures were made at 270° and 300° F. Recipes are given in Table I.

TABLE I

RECIPES OF STOCKS

Stock No.	I	II	III	IV
Crude Buna-S	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
Dibenzothiazyl disulfide	1.5	1.5	1.5	1.5
Bardol (softener)	5	5	5	5
Channel black	.	.	50	50
Sulfur	1	5	1	5

Physical tests were run by A.S.T.M. procedures. Sulfur determinations were made as outlined by Cheyney and Duncan[17]. Attempts were made to measure unsaturation of these stocks by the Kemp-Peters procedure[4]. This method was inapplicable to these samples for two reasons: *p*-Dichlorobenzene, the solvent they used, was not sufficiently active for some of these samples; and the use of acetone for purification of the sample before determination of unsaturation is believed unwise in general. In the latter connection, Cheyney and Robinson[18] and Kemp and Straitiff[7] noted that significant amounts of

vulcanizate are extracted out of various Buna-S by acetone. This is not surprising in view of the fractions of extremely low molecular weight reported in this polymer by the latter authors and by Sebrell[8].

The use of acetone for extraction is open to the further objection that it fails to remove soap which may be present in the crude polymer; this fact was noted by Kemp and Peters[4]. This is not a serious objection in a series where a given sample of polymer is used throughout. To compare samples of differing degrees of purity, it is desirable to use a solvent which removes as completely as possible nonpolymer material without removing polymer fractions. The writers have found that acetone is completely untrustworthy for this purpose; they have substituted ethanol, which is a solvent for the usual nonpolymer materials found in Buna-S, including soap, and is a complete nonsolvent for the polymer fractions themselves.

Whereas Kemp and Peters stated that *p*-dichlorobenzene will usually dissolve vulcanized Buna-S tread stocks within 3 hours, the channel black stocks investigated here did not dissolve even after 10 hours of continuous boiling in *p*-dichlorobenzene. When the samples were cut into paper-thin shavings with a razor blade, they dissoved after several hours of boiling in *p*-dichlorobenzene. Uncured and pure gum stocks dissolved without too much difficulty.

The method of solution finally adopted utilizes a phthalate plasticizer in combination with *p*-dichlorobenzene. Most of the determinations were made with either dibutyl phthalate or dioctyl phthalate, which were used interchangeably. Other ester plasticizers would probably be satisfactory. These phthalates aid in peptizing the vulcanized rubber sample without affecting the unsaturation of the latter, and show only a slight tendency to react with the iodine chloride reagent under the experimental conditions.

UNSATURATION MEASUREMENTS

The samples were passed through a cold, tight mill about thirty times to facilitate solution. This is believed to have no significant effect on iodine number, and Fisher[19] found that there is only a slight loss in unsaturation of pale crepe which had been milled 2 hours in air. The weighed sample (0.075 gram) was then extracted with alcohol for 16 hours, dried at 50° C under high vacuum, and kept in vacuum before analysis. The analysis was carried out within 24 hours after extraction to minimize any oxidative effects.

The sample was placed in a 250-cc. Pyrex stoppered iodine flask together with 5 cc. of phthalate, and 10 grams of *p*-dichlorobenzene was added. The flask was heated on a hot plate at about 180° C, with the stopper loosened. The sample swelled at first and then began to dissolve rapidly. In the case of the carbon-black samples this preliminary swelling period was about 30 minutes. During the succeeding 10 minutes the solution changed from colorless to black, and the sample became well dispersed.

To ensure complete solution, 35 additional grams of *p*-dichlorobenzene was added during this period of rapid solution, and heating was continued for another 30 minutes. Solution was facilitated by swirling the flask from time to time, with care to avoid allowing particles to stick to the sides. When the sample was in solution, the flask was slowly cooled to room temperature; 30 cc. of chloroform was then added, followed by exactly 25 cc. of standard iodine chloride (0.2 *N*) solution in carbon tetrachloride. The glass stopper of the flask was closed, and a thin film of 15 per cent potassium iodide solution was placed on it. The reaction solution was allowed to stand for one hour at room temperature. At the end of this time, 25 cc. of fresh 15% potassium iodide were

added, followed by 25 cc. of ethanol for the pure-gum stocks and 50 cc. for the carbon black stocks. Excess iodine was immediately titrated with standard 0.1 *N* sodium thiosulfate. Another 25 cc. of ethanol was added near the end of the titration to aid in breaking up the emulsions.

TABLE II

PROPERTIES OF BUNA-S VULCANIZATES

Stock No.	Curing temp. (° F)	Curing time (min.)	Gram combined S per 100 grams polymer	Iodine no.	Unsaturation (%)	Tensile strength (lb. per sq. in.)	300% modulus (lb. per sq. in.)	Elongation (%)
I	..	0	0.000	288	92.9	..	..	..
	270	20	0.176	271	87.5	75	..	775
		50	0.220	261	84.3	100	..	1000
		80	0.264	254	82.0	100	..	1125
		110	0.264	239	77.1	100	..	800
		140	0.264	232	74.9	100	..	500
	300	20	0.264	228	73.7	50	..	900
		50	0.352	217	70.0	150	..	350
		80	0.484	214	69.0	175	..	300
		110	0.564	205	66.2	200	..	250
		140	0.617	199	64.1	225	..	250
II	..	0	0.000	278	92.7	..	..	..
	270	20	0.766	251	83.7	100	..	1000
		50	1.617	244	81.3	175	..	600
		80	2.466	236	78.7	200	..	300
		110	3.148	232	77.3	225	..	250
		140	3.744	230	76.7	250	..	175
	300	20	1.786	220	73.3	150	..	300
		50	3.659	205	68.4	200	..	250
		80	3.957	196	66.4	200	..	200
		110	4.000	192	64.0	275	..	200
		140	4.000	194	64.7	200	..	175
III	..	0	0.000	199	92.7	..	..	..
	270	20	0.092	179	83.3	300	200	625
		50	0.182	170	79.0	1050	300	575
		80	0.245	165	76.8	1950	650	550
		110	0.275	162	75.3	2300	700	550
		140	0.335	152	70.7	2300	850	525
	300	20	0.366	162	76.3	1100	400	750
		50	0.488	160	74.4	2250	950	700
		80	0.488	158	73.5	2300	1250	650
		110	0.488	155	72.1	2300	1350	600
		140	0.488	153	71.1	2300	1400	575
IV	..	0	0.000	195	92.9	..	..	..
	270	20	1.195	167	79.5	800	750	325
		50	1.671	147	70.0	2700	1650	225
		80	2.030	110	66.6	2450	2400	200
		110	2.268	127	60.4	2250	..	200
		140	2.507	124	59.1	2000	..	200
	300	20	2.089	133	63.4	2300	..	700
		50	2.567	128	60.9	2500	..	450
		80	2.806	124	59.1	2450	..	300
		110	2.885	123	58.6	2400	..	250
		140	2.885	119	56.6	2350	..	200

A blank containing identical quantities of all reagents was taken through the same procedure. The iodine value is obtained by the calculation:

$$\text{Iodine no.} = \frac{\text{cc. thiosulfate (blank} - \text{sample)} \times 1.269}{\text{sample wt. in grams}}$$

All determinations were made in duplicate. The iodine numbers in Table II were the averages of these duplicate determinations. Theoretical unsaturation for each stock was calculated on the basis of a 75 per cent butadiene—25 per cent styrene content for the hydrocarbon portion of the crude polymer. The iodine number is thus three fourths of that of polybutadiene, or 352. For each of the four stocks, the percentage unsaturation was then obtained by multiplying this figure by the percentage polymer in the stocks. The theoretical values of iodine number for the four stocks are thus 310, 300, 215, and 210, respectively.

Each value of iodine number was converted to percentage unsaturation by a simple calculation (Table II). The four uncured stocks show excellent agreement at about 93 per cent of theoretical. The remainder is presumably non-rubber material, with perhaps some diminution due to branch chaining, etc.

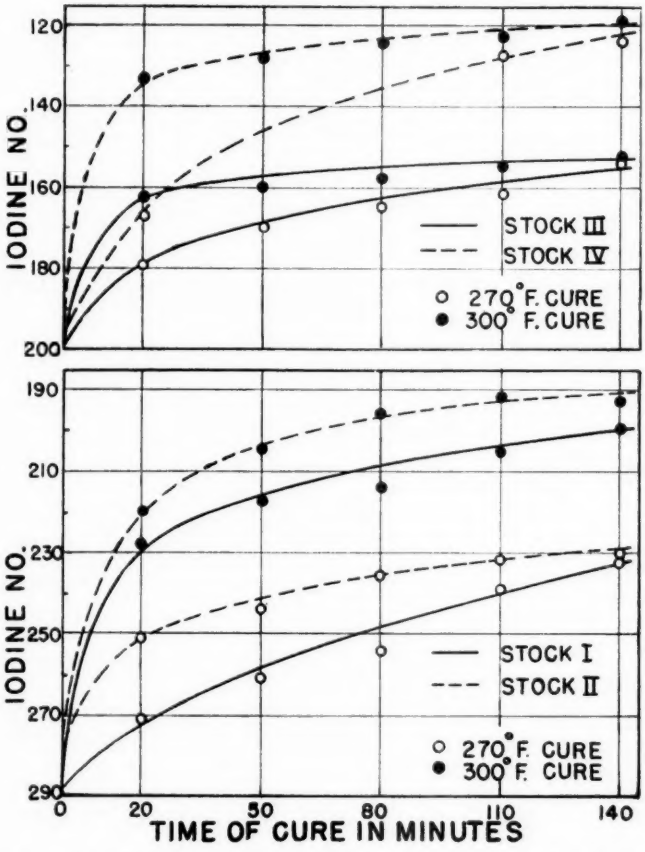
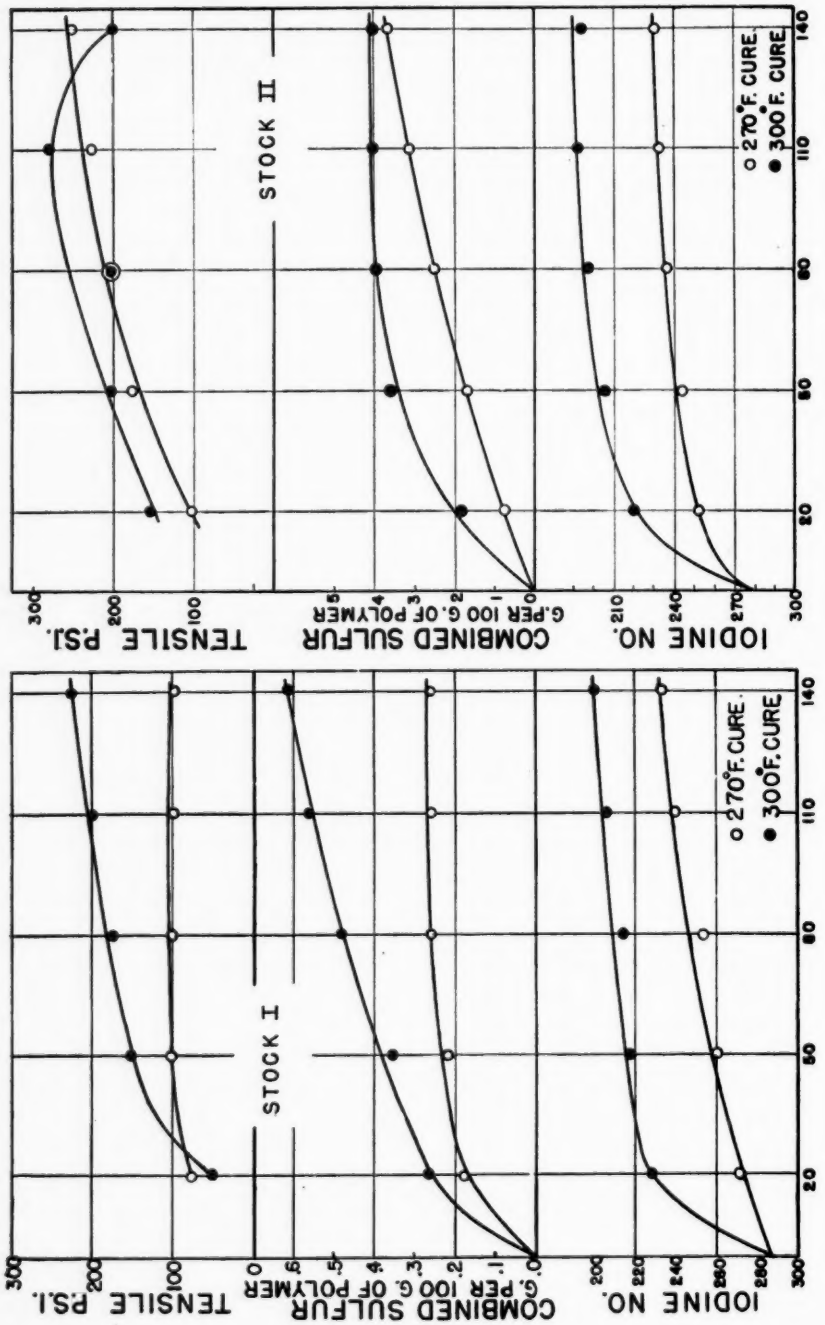


FIG. 1.—Curing Time *vs.* Unsaturation for Channel Black and Pure Gum Stocks


STOCK II
STOCK I
TENSILE P.S.I.
COMBINED SULFUR
G. PER 100 G. OF POLYMER
IODINE NO.
o 270°F. CURE.
• 300°F. CURE.

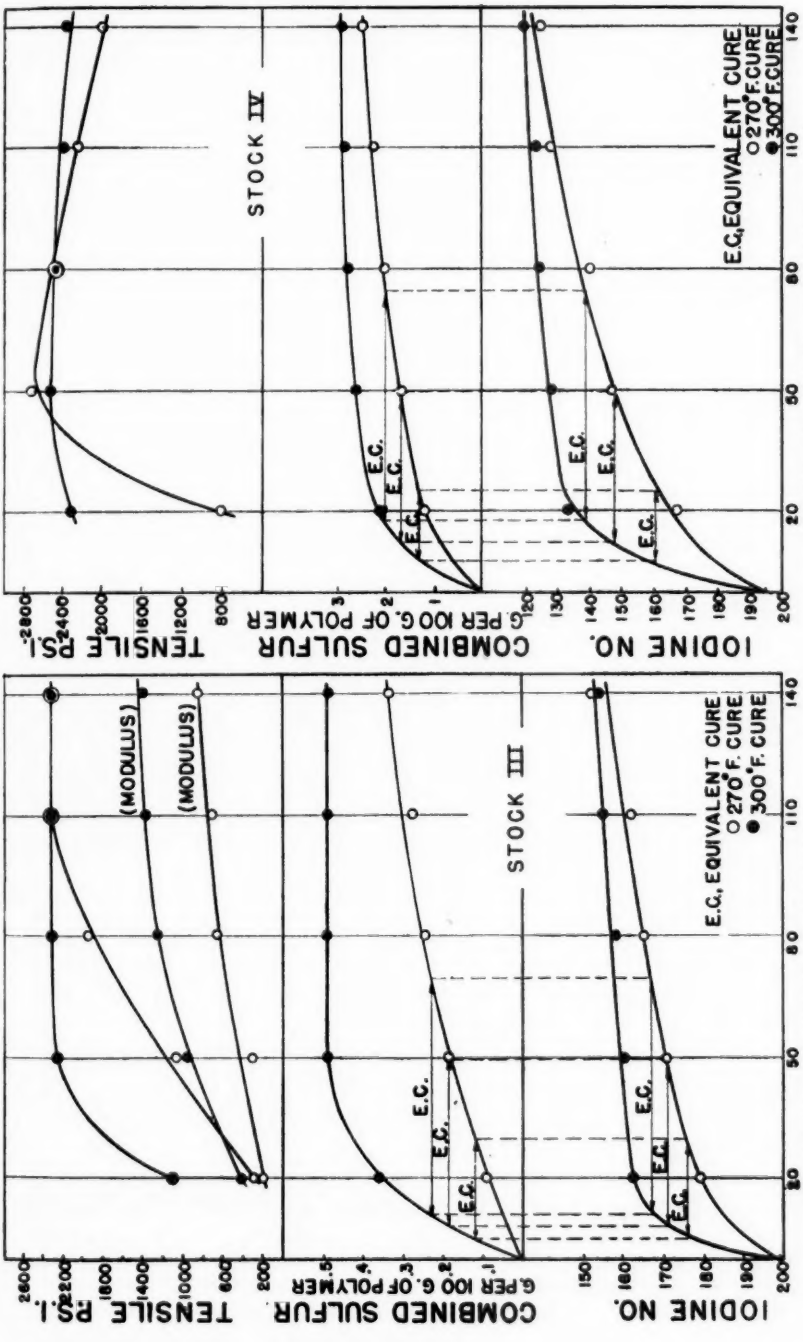


FIG. 2.—Effect of Cure on Properties of the Four Stocks

This value is in excellent agreement with that of Kemp and Peters, who used an average value of 93 per cent hydrocarbon content in the crude polymer.

EFFECTS OF VULCANIZATION

The experimental data in Table II are recorded graphically in Figures 1, 2, and 3. Temperature relations are what might be expected from previous data. Higher temperature results in a more rapid decrease in unsaturation, just as it results in a more rapid combination of sulfur and a more rapid increase of tensile strength. The reaction is most rapid in the first part of the cure and then tapers off. Unsaturation appears to approach a limiting value, although it had not positively reached this limit in any of the samples studied. There is some indication that this limit might be the same for the 270° and 300° F stocks, at least for the reinforced stocks.

In the channel black stocks the rapid part of the reaction is considerably faster than in the pure gum stocks. Two factors may be involved: (1) The heat requirement for a given state of reaction may be largely required for the rubber-sulfur-accelerator system; a loaded stock containing only two-thirds as much rubber as the corresponding pure-gum stock would thus be expected to require roughly two-thirds as much heat to reach a given state of cure. (2) The large amount of pigment in the loaded stock makes possible a rapid transfer of heat through the stock and thus facilitates a much more rapid cure. It should be noted that this effect is different from that usually reported for natural rubber systems, where carbon black exerts a retarding action on cure.

The 5 per cent sulfur stock at a given temperature approaches a limiting iodine value lower than that of the corresponding 1 per cent sulfur stock. Since the combined sulfur is greater in the 5 per cent stock, some relation between combined sulfur and iodine value is indicated.

The matter of "equivalent cures" is indicated in Figure 2 for stocks III and IV. Here it is apparently possible to obtain an equivalent state of cure for the same stock at two different temperatures, as shown by both combined sulfur and unsaturation. There is, however, no such simple relation with tensile strength. Furthermore, this relation holds true over a limited range and, apparently, only for the reinforced stocks.

Elongation data are included in Table II. No curves are shown because the graphical character of this property was shown previously[18]. The elongation goes through a maximum in the early stages of the cure, then decreases rapidly, and levels off at a fairly constant value. Significantly, the maximum elongation is reached more rapidly in the channel black stocks. However, this maximum seems to bear no simple relation to any of the other properties studied, as combination of sulfur, decrease of unsaturation, and increase of tensile strength all continue after the maximum elongation has been passed. The shape of the elongation curve may have some structural significance; there are insufficient data in this report to indicate what this significance may be.

It is of interest to determine how sulfur combination and loss of unsaturation are related on a theoretical basis. Brown and Hauser's general procedure of plotting unsaturation against combined sulfur is employed in Figure 3. The dotted lines represent the theoretical relation if each double bond removed were the result of combination with one or two atoms of sulfur. The solid lines represent experimental values. Whereas the natural rubber stocks investigated by Brown and Hauser indicated, in general, from one to two atoms of sulfur combined per double bond lost, the significant characteristic of the

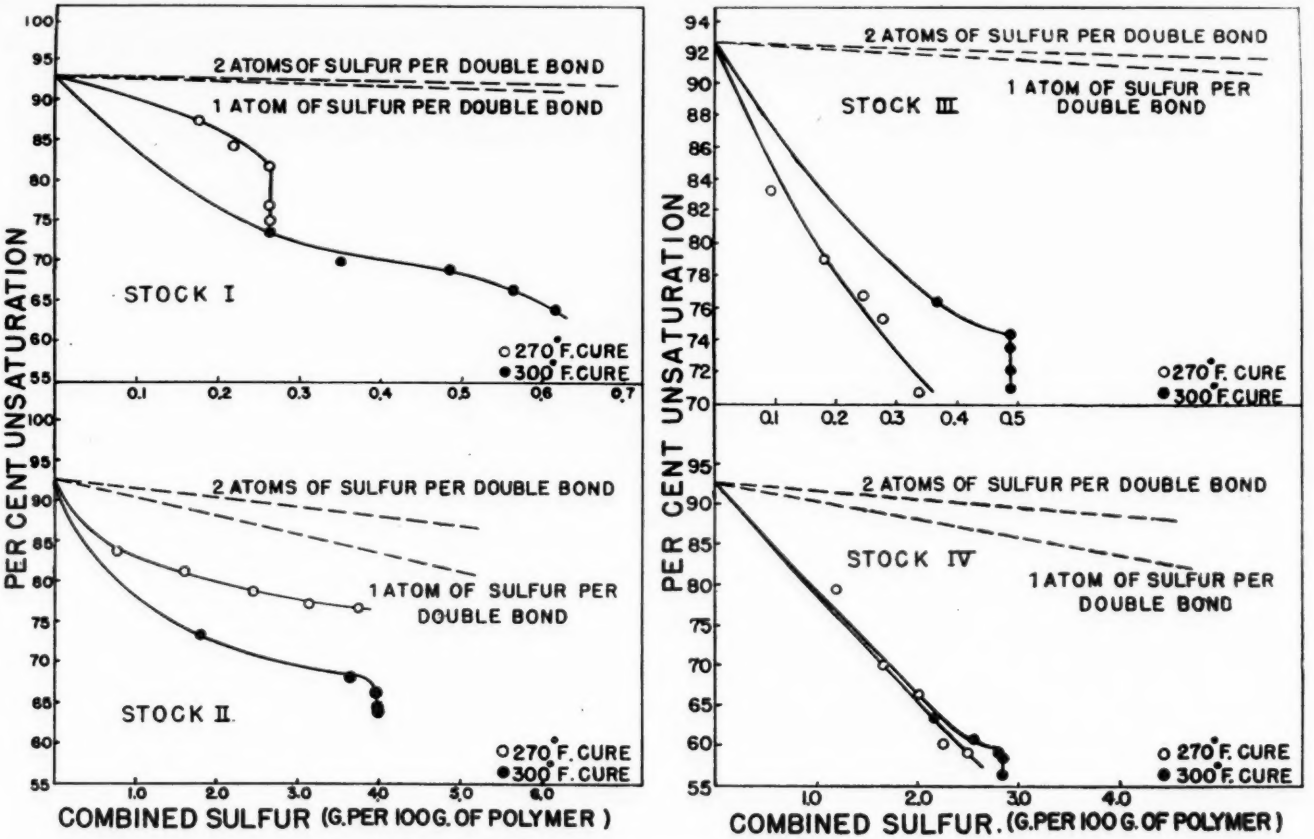

2 ATOMS OF SULFUR PER DOUBLE BOND
1 ATOM OF SULFUR PER DOUBLE BOND
STOCK I
○ 270° F. CURE
● 300° F. CURE
2 ATOMS OF SULFUR PER DOUBLE BOND
1 ATOM OF SULFUR PER DOUBLE BOND
STOCK II.
○ 270° F. CURE
● 300° F. CURE
PER CENT UNSATURATION
COMBINED SULFUR (G. PER 100 G. OF POLYMER)
2 ATOMS OF SULFUR PER DOUBLE BOND
1 ATOM OF SULFUR PER DOUBLE BOND
STOCK III
○ 270° F. CURE
● 300° F. CURE
2 ATOMS OF SULFUR PER DOUBLE BOND
STOCK IV
1 ATOM OF SULFUR PER DOUBLE BOND
○ 270° F. CURE
● 300° F. CURE
PER CENT UNSATURATION
COMBINED SULFUR. (G. PER 100 G. OF POLYMER)

FIG. 3.—Change in Unsaturation *vs.* Combined Sulfur for the Four Stocks.

data reported here is the abnormally high loss of unsaturation in relation to combined sulfur.

Sulfur is obviously combining with polymer, but some second reaction is also obviously a part of the vulcanization process. It may be possible that two relatively unrelated reactions are taking place. The primary reaction involving sulfur may not even involve the double bond. It may be a substitutive reaction at the alpha carbon, as postulated by Farmer. This may involve dehydrogenation with the formation of hydrogen sulfide, which could add to the double bonds, or it may involve allylic shifts like those reported by Armstrong, Little, and Doak.

The remaining reaction involving the double bonds is presumably a polymerization type, as suggested by Whitby[20] and by Brown and Hauser. There is a possibility that double bonds may be removed by reaction with oxygen, as well as by direct carbon-to-carbon polymerization. The two main reactions apparently bear a relatively constant relation, as evidenced by the linear relation between combined sulfur and loss of unsaturation in Figure 3. When the sulfur combination is complete, the decrease in unsaturation continues and indicates some additional type of reaction, presumably also polymerization in nature, which continues on overcure. Since this probably involves crosslinking between chains, it would result in an increase of rigidity; this is in agreement with the observed continued increase of modulus on overcure of such Buna-S stocks.

Thornhill and Smith[21] showed that sulfur combines with natural rubber-carbon black stocks without loss of unsaturation. The high loss of unsaturation reported here may be evidence that the mechanism of vulcanization is totally different for the two materials. It may be possible that the alpha carbon is not involved in the primary vulcanization reaction of Buna-S.

CONCLUSIONS

In conclusion, the data presented here indicate that two types of chemical reactions take place during the vulcanization of Buna-S stocks of a specific type: (1) a combination with sulfur, which may or may not involve the double bonds in the polymer, and which may be similar in character to the primary vulcanization reaction of natural rubber; (2) a second reaction, presumably polymerization, which accompanies the first and is related to and possibly initiated by it, and which continues on overcure.

ACKNOWLEDGMENT

This material included in this paper is taken from a thesis submitted by Max H. Keck in partial fulfillment of the requirements for the degree of Master of Science at the University of Akron. A considerable portion of the experimental work was carried out in the Goodyear Research Laboratory; thanks are due L. B. Sebrell for this privilege.

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EFFECT OF PRESSURE ON THE MELTING OF CRYSTALLINE RUBBER *

LAWRENCE A. WOOD AND NORMAN BEKKEDAHL

NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.

AND

RALPH E. GIBSON

GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION, WASHINGTON, D. C.

INTRODUCTION

The effect of hydrostatic pressure on the melting of crystalline rubber has been the subject of a brief investigation extending to pressures above 1,000 atmospheres. With a particular sample of stark rubber it was found possible to raise the temperature of melting, as determined by the disappearance of birefringence, from about 36° to 70° C by the application of a pressure of 1,170 bars ($1{,}170 \times 10^6$ dynes per sq. cm.). The results, including observations at intermediate pressures, are given in Table 1 and in Figure 1.

TABLE 1

PRESSURE AND RELATED QUANTITIES AT TEMPERATURE OF MELTING

Temperature of melting	Pressure		dT/dp calculated	$L/\Delta V$, calculated
	Observed	Calculated		
°C	*Bars*	*Bars*	*deg C/bar*	*j/cm³*
36.2	—	1	0.0365	846
40	106	108	0.0345	906
45	259	258	0.0323	987
50	433	419	0.0302	1,060
55	586	590	0.0283	1,160
65	967	966	0.0250	1,350
70	1,170	1,172	0.0236	1,450

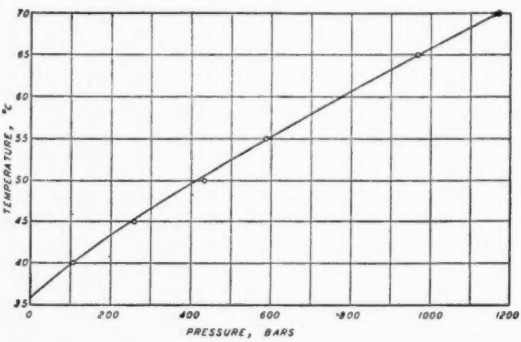

FIG. 1.—Relation between temperature of melting and applied pressure for a sample of stark rubber.

* Reprinted from the *Journal of the National Bureau of Standards*, Vol. 35, No. 11, pages 375–380, November 1945. This paper was published also in *The Journal of Chemical Physics*, Vol. 13, No. 11 pages 475–477, November 1945.

SAMPLE

The crystalline smoked-sheet sample, called stark rubber, as it had a melting range above room temperature, was furnished in 1939 by H. I. Cramer while he was a professor at the University of Akron.

Melting of a portion of this sample at atmospheric pressure was determined from observations of volume changes in a mercury-filled dilatometer by a method previously described[1]. It can be seen from the temperature-volume relation shown in Figure 2 that melting occurred over a range of temperature from 32° to 39° C. The disappearance of the birefringence, which according to Figure 1 takes place close to 36° C at atmospheric pressure, evidently defines a position near the center of the melting range.

The expansivity $(1/V)(dV/dT)$ at 25° C of the amorphous rubber calculated from data plotted in Figure 2 is found to be 650×10^{-6} per degree centigrade and that of the crystalline rubber 590×10^{-6} per degree centigrade.

APPARATUS AND PROCEDURE

The high-pressure equipment used in this investigation was located in the Geophysical Laboratory of the Carnegie Institution of Washington, and has been described in previous papers[2]. The approximate adjustment of the pressure was made by means of a hand pump and the fine adjustment by a screw plunger operated by a wheel. The amount of pressure was determined by a calibrated manganin wire resistance-gauge[3].

Specimens of the stark rubber sample were cut into strips about a millimeter in thickness. One strip of this stark rubber and a similar strip previously melted by heating to about 70° C were placed side by side in a glass piezometer. The use of two specimens adjacent to each other permitted an excellent visual criterion for determining when birefringence disappeared.

Ethylene glycol was used as a confining liquid in the piezometer. Water was found to be unsatisfactory for this purpose, since it penetrated the rubber specimens and impaired their transparency after several hours at high pressures. No such difficulty was encountered with ethylene glycol.

Light from a 6-volt, 32-candlepower lamp, after being polarized by a sheet of Polaroid, passed through the window of the pressure equipment and through the specimen. The polarized light was observed, after emerging from the equipment, by the use of a second sheet of Polaroid as analyzer.

In operation, the piezometer containing the specimens was placed in the apparatus, the pressure was increased to about 1,300 bars, and the temperature of the bath was raised to the desired value. After temperature equilibrium was attained, the pressure was slowly lowered and continuous observations were made of the birefringence. Except during the melting of the stark specimen, no significant variation with pressure was noted in the appearance of the birefringence of the two specimens between crossed Polaroids.

RESULTS AND DISCUSSION

The change in birefringence associated with the melting of the stark specimen was found to take place over a small range of pressure, with the major portion of the change occurring within an interval of only a few bars. The pressure at which the change of birefringence was most rapid has been used as abscissa in Figure 1, and the corresponding bath temperature as ordinate. A new specimen, cut from the same sheet of stark rubber, was required for each

point. The data from which the curve was plotted are given in the first two columns of Table 1.

The relation between the temperature of melting and the pressure shown by the curve cannot be regarded as valid for crystalline rubber having at atmospheric pressure a melting range different from that described here. As the melting range at atmospheric pressure depends on the temperature at which the crystals were formed[4], this fact limits the application of the present results. However, if a study were to be made of rubber crystallized at different temperatures, it is presumed that as a first approximation a family of curves not too far from parallel would be obtained, with displacement along the temperature axis

Some crystallization was observed when amorphous specimens were kept under a pressure of about 1,100 bars at 30° C for 16 hours. It was observed that the crystals formed in this manner melted at a much lower temperature than the value for the same pressure given by the curve in Figure 1. The crystals formed under these conditions were evidently different from those present originally in the stark rubber. At atmospheric pressure the temperature of melting, as already mentioned, depends on the temperature at which the crystals were formed. No doubt the melting depends in a somewhat similar fashion on the pressure on the rubber during crystallization.

At atmospheric pressure rubber crystallizes at temperatures between −50° C and +15° C, crystallizing most rapidly at temperatures near −25° C. The effect of an increase of pressure is to raise the range of temperatures at which crystallization may occur. For example, Thiessen and Kirsch[5] found that pressures up to 25 atmospheres increased the rate of crystallization at temperatures near 10° C. Dow[6] observed that a pressure of 8,000 kg. per sq. cm. raised the range of temperature favorable for crystallization so much that no crystals were formed during 14 days at 0° C. The partial crystallization after 16 hours at 30° C under a pressure of 1,100 bars in the present work is additional evidence of the same effect

The curve shown in Figure 1 can be represented adequately by the three-constant logarithmic equation:

$$\log_{10}(p + 1{,}300) = 5.9428 - \frac{875}{T}$$

where T is the temperature of melting in degrees Kelvin and p is the pressure in bars. The values given in the third column of Table 1 are calculated from the above equation. A differentiation of the equation gives:

$$\frac{dT}{dp} = \frac{T^2}{2{,}015(p + 1{,}300)}$$

from which the values in the fourth column of the table were calculated.

The use of the Clapeyron equation:

$$\frac{dp}{dT} = \frac{L}{T\Delta V}$$

where L is the heat of fusion and ΔV the corresponding change in volume, makes possible a calculation of $L/\Delta V$ from the data just given. This quantity, in joules per cubic centimeter of volume change, is shown in the last column of the table.

From the dilatometric measurements represented by the graph in Figure 2, ΔV was found to be 0.0191 cc. per gram of rubber at 36.2° C. From these data the value of L for this sample is calculated to be 16.2 j. per gram.

Other observations in this laboratory have shown that this sample of stark rubber could undergo additional crystallization at lower temperatures. The full heat of fusion should include the contribution of these additional crystals, which were observed to form at the lower temperatures. Therefore, we do not regard the value just given as the full heat of fusion of crystalline rubber at 36.2° C. A direct measurement[7] of the heat of fusion of another sample of rubber melting over a range centered at about 11° C yielded 16.7 j. per gram. The corresponding value at 36.2° C might be expected to be larger than that at 11° C. The terms ΔV and T in the Clapeyron equation are both larger at the higher temperature, but a lack of data regarding the values of $(dp)/(dT)$ at 1 bar for samples melting between 11° and 36.2° C prevents drawing a definite conclusion. In spite of the impossibility of making an exact calculation with the data available, the agreement in order of magnitude is quite satisfactory.

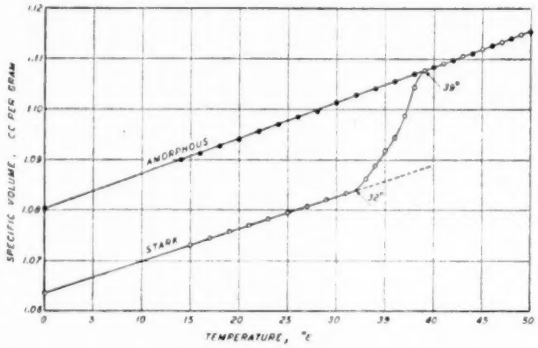

FIG. 2.—Relation between specific volume and temperature at atmospheric pressure for the sample of stark rubber, before and after melting.

The rate of change of melting temperature with pressure is observed to have the value of 0.037 degree centigrade per bar at the lowest pressures and to decrease with increasing pressure to a value of about 0.024 degree centigrade per bar at 1,170 bars. The average value over the range studied is 0.029 degree centigrade per bar. This is considerably lower than the average value calculated from a single observation of Dow[6], who found rubber crystallized at 0° C to melt at 77.5° C under a pressure of 1,270 kg. per sq. cm. From this observation one may calculate a value of 0.052 degree centigrade per bar if 11° C is taken as the melting temperature at atmospheric pressure for rubber crystallized at 0° C[8].

The experimental observations for the present investigation were made in the summer of 1940, but earlier publication was prevented by war activities, which also led to the abandonment of a more extensive investigation that had been planned.

SUMMARY

The effect of hydrostatic pressure on the melting of crystalline rubber has been the subject of a brief investigation extending to pressures above 1,000 atmospheres. With a particular sample of stark rubber, it was found possible

to raise the temperature of melting, as determined by the disappearance of birefringence, from about 36° to 70° C by the application of a pressure of 1,170 bars ($1{,}170 \times 10^6$ dynes per sq. cm.). The results, including observations at intermediate pressures, can be represented adequately by the equation: $\log_{10}(p + 1{,}300) = 5.9428 - (875/T)$.

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SURFACE FILM THICKNESSES OF POLYMERIC SUBSTANCES IN RELATION TO MOLECULAR STRUCTURE *

FREDERICK T. WALL AND MURRAY ZELIKOFF

NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

It is well known that certain compounds, such as long chain fatty acids, can form monomolecular films on water and that the areas of such films can be related to the dimensions of the molecules[1]. Certain polymeric substances, including cellulose derivatives[2], proteins[3] and the polymer of ω-hydroxydecanoic acid[4] likewise form stable films whose areas can be conveniently measured[5]. At this time we wish to report that we have prepared films of some rubberlike polymers as well, and that the results appear to give useful information about their molecular structures, particularly in relation to branching.

Five cc. of a very dilute benzene solution of a polymer ($c = 2 \times 10^{-6}$ g. per cc.) is distributed over the water surface of a hydrophil balance. After the benzene has evaporated, the film area is measured in the usual manner[6]. Low conversion samples of GR-A (butadiene-acrylonitrile copolymer) gave films about 6 Å. thick, whereas high conversion samples exhibited thicknesses as great as 30 Å. It is our belief that a large film thickness indicates a high degree of branching and that the corresponding polymer molecules can be better represented as "bottle brushes" than as straight chains. Other polymers containing hydrophilic groups have also been investigated; these include copolymers of butadiene with methacrylonitrile, 1-cyanobutadiene, *m*-fluorostyrene and some vinylpyridines.

Stable films for polymers such as natural rubber or GR-S could not be obtained directly. However, these substances can be investigated by the film technique if they are first rendered hydrophilic by the addition of thiocyanogen to some of the double bonds according to the methods of Pummerer and Stark and of Rehner[7]. After using their procedures, we found natural rubber and gutta-percha to form relatively thin films (about 8 Å. thick), whereas the film thicknesses of GR-S exhibited wide variations with polymer conversion, indicating once more marked differences in branching.

On the whole, the method appears to show considerable promise as a tool for learning more about the structure of polymers.

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* Reprinted from the *Journal of the American Chemical Society*, Vol. 68, No. 4, page 726, April 1946. The work reported in this letter was done in connection with the Government research program on synthetic rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation (results first reported in November, 1945).

EFFECTS OF MOLECULAR STRUCTURE ON PHYSICAL PROPERTIES OF BUTYL RUBBER *

PAUL J. FLORY

ESSO LABORATORIES, STANDARD OIL DEVELOPMENT COMPANY, ELIZABETH, N. J.

It is now generally agreed that vulcanized rubber possesses a network structure made up of cross-linked long-chain molecules. During vulcanization the cross-linkages, consisting of primary valence bonds of one sort or another, are introduced at occasional junctures between the essentially linear polymer molecules of the raw rubber, natural or synthetic. In this process the soluble, semiplastic raw rubber is converted to an inherently insoluble, nonplastic material of high strength and durability. This drastic change in properties is attributed to the network structure which emerges as a consequence of the cross-linkages. The almost total insolubility of the vulcanized rubber indicates that nearly all the raw rubber molecules become a part of the network, which extends throughout the piece of rubber. Various lines of evidence show that only a minute fraction of the structural units of the primary rubber molecules enter into cross-linkages.

Whereas this qualitative concept has gained almost undisputed acceptance, its logical extension toward quantitative formulation of the network structure has not been carried through. Progress in this direction has been hampered by a lack of suitable experimental methods and theoretical principles pertaining to polymeric network structures. It is obvious that the two basic variables which characterize the network structure are (1) the lengths or molecular weights (including the molecular weight distribution) of the primary rubber molecules, and (2) the frequency, or concentration, of cross-linkages between them. Neither of these has been subjected to systematic quantitative evaluation in rubber vulcanizates.

Recent advances in structural chemistry of high-polymer systems made it evident at the beginning of this investigation that both of these quantities which characterize the network structure should be amenable to quantitative measurement. The lengths of the primary molecules of which the vulcanizate is composed can be established by determining the molecular weight immediately preceding vulcanization. Methods for the measurement of molecular weights of high polymers have been developed within the past few years which obviate any serious difficulty in this phase of the problem. Determination of the concentration of cross-linkages presented greater difficulties. The conventional process by which the cross-linkages are introduced (sulfur-accelerator vulcanization) clearly is not a simple chemical reaction[1] from which their number could be deduced from chemical analysis or stoichiometric relations. Indirect determination of the degree of cross-linking is feasible, however, with the

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 38, No. 4, pages 417–436, April 1946. The present address of the author is The Goodyear Tire & Rubber Co., Akron, Ohio.

aid of recently developed theoretical treatments of the process of network formation[2].

Once the basic structure of vulcanized rubbers can be subjected to quantitative measurement, a new approach to the understanding of the physical properties of rubbers can be realized. It then becomes possible to establish relationships between physical properties and vulcanizate structure, a field which has been neglected in the past.

Of the various known vulcanizable rubberlike polymers, Butyl[3], a copolymer of isobutylene with a very small percentage of a diolefin, is best suited to an investigation of the type described here. Its chemical stability, particularly toward oxidation, permits the necessary operations involved in the separation of the polymer into fractions of narrow molecular weight range to be carried out without degradation or other chemical changes. The fractions so obtained can be mixed with compounding ingredients on a mill in a conventional manner without encountering an intolerable degree of breakdown. Thus, the characteristic molecular weight and structure of the sample can be preserved up to the vulcanization step. The susceptibility of natural rubber to oxidative degradation and to mechanical breakdown would render the execution of a similar investigation on this substance exceedingly difficult if not impossible. GR-S and certain other synthetic rubbers undergo other oxidative changes which might be equally disruptive. Deviations from linearity in the structures of their primary molecules adds a further complication not encountered with Butyl rubber.

A further merit of Butyl for the purposes of the present investigation is the facility with which the degree of cross-linking can be controlled by manipulating the amount of diolefin introduced into the polymer during synthesis. Finally, it possesses many of the physical properties of natural rubber, concerning which there is a greater background of fundamental information than for any other rubberlike material. Such properties include[3] high tensile strength, both with or without carbon black, the ability to become highly crystalline when stretched, and a simple linear chain structure.

MICRO COMPOUNDING AND TESTING

To eliminate the effects of molecular weight heterogeneity, or at least to suppress them sufficiently, it was necessary to employ carefully fractionated samples of Butyl rubber in most of the work. Effective fractionation requires the use of very dilute solutions[4]; hence, the size of the individual fractions obtained is limited by the volume of solution which can be handled. Conventional compounding and testing methods require a minimum of 50 grams of rubber, a quantity considerably beyond the range of laboratory fractionation. It was necessary, therefore, to devise compounding and testing procedures applicable to fractions of the maximum size which it was practical to prepare by laboratory fractionation—*i.e.*, about 10 grams.

These micro compounding and testing procedures are essentially adaptations of the conventional methods employed with larger samples. [In this connection, the small scale evaluation procedures described by Garvey[5] are intermediate between our micro methods and those usually employed.] Within the range of the experience gained in the present work, no significant disadvantages in the micro methods have become apparent; furthermore, less space is required and the equipment is less expensive than that for the standard procedures. Tests on equivalent vulcanizates demonstrate that the micro procedures for compounding, curing, and testing of tensile strength and modulus

are at least as accurate and reproducible as the conventional methods; the results obtained by the two procedures are approximately the same.

Compounding.—All ingredients were weighed on an analytical balance and mixed on a 3 × 8 inch laboratory mill equipped with a movable center guide[5]. This guide was placed at a distance from the end guide, depending on the size of the sample, such as would assure a small bank at a mill-roll setting of 0.010 to 0.015 inch. By placing the center guide only 0.5 inch from the end, less than 2 grams of rubber could be compounded. Compounding ingredients were added immediately to the rubber after banding on the mill. The batch was cut six times from each side during a 10-minute milling period; then it was sheeted off and reweighed.

The mill rolls were maintained at about 130° F during compounding of the high-molecular-weight fractions (above about 200,000). At low temperatures breakdown becomes excessive. Fractions of lower molecular weight which were too plastic to handle on warm rolls, could be milled at 70° F without breakdown. Below a molecular weight of about 70,000 the material was too plastic to be handled even on cold mill rolls. Such fractions were mixed by hand in a polished iron mortar, which was heated to about 170° F.

The marked effect of temperature on breakdown of Butyl appears to be due to crystallization under the intense shearing conditions encountered on the mill. Crystallization renders the rubber much less plastic and thereby increases greatly the shearing stresses, which become sufficient to cause rupture of the chains. Elevation of the temperature eliminates the tendency of the rubber to crystallize under deformation, and breakdown is diminished.

Vulcanization.—Micro tensile sheets were cured in molds, 2.5 inches long and 0.025 inch thick, and either 1 or 1.75 inches wide. The former required a minimum of about 1.6 cc., and the latter about 2.5 cc. of stock, allowing for overflow. Dumbbells having the dimensions shown in Figure 1 were cut from

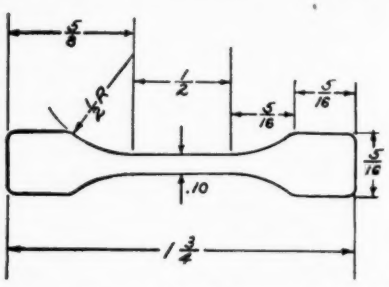


FIG. 1.—Dimensions of tensile dumbbell (in inches).

the sheets. Three could be cut from one of the former, and six from one of the latter. Rings suitable for stress-strain measurements were molded 1.025 inches in outside diameter, 0.050 inch thick, and either 0.10 or 0.25 inch wide. Thus, from as little as 3.5 cc. of rubber, two cures could be obtained, each to furnish three test dumbbells. An additional gram was required for two rings for stress-strain measurements.

Recipes.—The following recipe was employed in all pure gum compounds:

Butyl	100 parts
Sulfur	1.5
Zinc oxide	1.0
Tetramethylthiuram disulfide	1.0

The recipe for the compounds containing 50 parts of carbon black was as follows:

Butyl	100	Zinc oxide	5.0
Channel black	50	Tetramethylthiuram disulfide	1.0
Sulfur	2.0		
Stearic acid	3.0		

These recipes were chosen somewhat arbitrarily. They are not necessarily the best from the standpoint of optimum tensile strength or maximum modulus.

Polymers having different degrees of unsaturation were cured with the same proportions of ingredients. A rather large amount of evidence (to be shown later) indicates that, for a given recipe, the percentage utilization of unsaturation in the formation of cross-linkages is almost independent of the degree of unsaturation over a wide range. Doubling the proportions of sulfur, zinc oxide, and accelerator in the pure gum recipe affects the moduli and swelling ratios of rubbers of different unsaturations (cured 60 minutes) by factors which are about the same:

Approx. mole-percentage diolefin	Receipe	Modulus at 300 per cent, (lb. per sq. in.)	Swelling ratio
0.5	Standard	78	8.05
	Double	99	7.13
	Ratio	1.27	1.13
1.0	Standard	116	6.45
	Double	149	5.50
	Ratio	1.28	1.17

Hence, the influence of diolefin content *per se* is obtained with the least ambiguity by fixing the curing recipe.

This recipe was selected rather than one containing a greater proportion of curing ingredients because of the lower sensitivity to time of cure. An effort was made to cure (at 307° F) for times which yield approximately the maximum degree of cross-linking as judged by modulus or swelling. For the low-unsaturation Butyl rubbers this stage is reached at about 60 minutes; from 30 to 40 minutes are required for the high-unsaturation Butyls. Excessive times of cure lead to gradual "reversion" which we presume to be due to a competing degradative process.

Physical Testing.—Tensile strengths were measured on a Scott X-5 pendulum-type tester equipped with hinged roll clamps; the rolls were 0.25 inch in diameter. Through the use of different weights on the pendulum, any one of four scale ranges, from 0 to 2, 5, 10, or 20 pounds, could be employed. The rate of extension was about 6 inches per minute. This is less than the A.S.T.M. specification of 20 inches per minute, but the greater part of this difference is justified by the difference in length of our dumbbell as compared with that recommended by the A.S.T.M. Elongations were estimated from the distance between marks, initially 0.50 inch apart, as measured with a ruler.

Stress-strain curves were determined on the same instrument, equipped with ring test spools 0.25 inch in diameter and a scale for indicating the distance of separation of the spools. Both spools were mounted in roller bearings, the lower one being rotated by a chain and sprocket in order to ensure even distribution of strain over the rubber ring. The rate of separation corresponded to about 300 per cent elongation per minute. A spark recording of the tension scale reading was taken at regular elongation intervals.

Swelling Measurements.—A modification of the method employed by Whitby, Evans, and Pasternack[6] was used. Fragments from the tensile sheets or rings amounting to about 0.2 gram, weighed to ±0.2 mg., were placed with 50 cc. of C.P. cyclohexane containing 0.01 per cent phenyl-β-naphthylamine in a glass-stoppered weighing bottle. After standing 48 hours in the dark at room temperature, the swollen samples were placed in a weighing bottle containing filter paper to blot off excess solvent. The bottle and contents were weighed, the sample was removed, the stopper was replaced, and the bottle and moist filter paper were reweighed. The difference represents the weight of swollen polymer. The percentage of soluble components was determined by evaporating the cyclohexane solution to dryness and weighing the residue. The weight of phenyl-β-naphthylamine was deducted. The weight of rubber in the swollen vulcanizate was taken as the difference between the original sample weight and the weight of the extractable material.

The volumes of rubber and solvent in the swollen sample were calculated from their respective weights and their densities at 25° C (0.93 for the pure-gum Butyl compounds). The swelling ratio is expressed as the ratio of the total volume of swollen sample to the volume of dry (insoluble) rubber it contains.

Creep Measurements.—Square-end dumbbells, 0.100 inch wide over a 1.5-inch length, were cut with a die from the tensile sheets (T-50 test specimen). The sample was suspended at one end, and a weight was attached to the other. Reference points for measuring relative lengths were provided by piercing the sample with short wires 0.015 cm. in diameter at points about 3.5 cm. apart within the uniform section of the test-piece. The distance between the upper edges of these wires was determined with a measuring microscope equipped with a scale reading to ±0.001 cm. All tests were run in a constant-temperature room regulated at 25.0 ± 0.3° C.

Fractionation.—Details concerning the fractional precipitation procedure for the isolation of samples of narrowed molecular weight range were described previously[7]. One hundred grams (in a few cases, 50 grams) of the crude Butyl rubber were dissolved in 10 liters of thiophene-free benzene. Sufficient acetone to precipitate the first fraction at 25.0° C was added, and the solution was warmed sufficiently to reach homogeneity. Precipitation was allowed to occur while cooling slowly to 25.0° C with mild agitation. After the precipitated phase had settled, the liquor was poured off and set aside. The precipitate was redissolved in 6 liters of benzene and reprecipitated as before, using the same proportion of acetone to benzene. After separating the liquor, this precipitate was coagulated and dried in vacuum at 70° C. The liquors were combined, evaporated to remove acetone, made up to 10 liters with benzene, and a slightly larger quantity of acetone was added to obtain the second fraction, which was reprecipitated in the manner mentioned above. After most of the polymer had been separated in the form of fractions, the volumes of benzene used in each step were reduced. Proceeding in this way, a series of some ten fractions of progressively smaller molecular weights was obtained from each polymer. To assure good fractional separations[8], polymer concentrations not exceeding 1.0 per cent were used in the first precipitation of each fraction, and around 0.3 per cent in the reprecipitation of high-molecular-weight fractions.

CHARACTERIZATION OF POLYMERS AND FRACTIONS

Raw Polymers.—The Butyl polymers were prepared by copolymerization of isobutylene with small proportions of isoprene at low temperature[3]. Their

intrinsic viscosities (Table I) were computed from the viscosities of their dilute solutions in diisobutylene at 20° C. "Intrinsic viscosity" as here employed is defined by the equation[9]:

$$[\eta] = (\ln \eta_r)/c$$

where η_r is the relative viscosity of a solution of concentration c (in grams per 100 cc.) such that η_r is less than about 1.4, but greater than about 1.15 to assure sufficient precision in the value of intrinsic viscosity. The molecular weights were calculated from the intrinsic viscosities by means of Equation 1.

The mole percentages of diolefin units, or percentage unsaturation values (last column of Table I) were obtained by the ozonolysis method of Rehner[10].

TABLE I

CHARACTERISTICS OF CRUDE BUTYL POLYMERS FROM WHICH FRACTIONS WERE SEPARATED

Polymer designation	Intrinsic viscosity $[\eta]$	"$\overline{M}_v$" $\times 10^{-3}$	Mole-per cent diolefin units detd. by ozone degradation[a]
I	2.20	820	0.43
II	1.32	370	0.54
II-A	1.45	425	0.53
III	0.67	130	0.48
IV	0.73	145	1.05
V	1.18	310	1.2

[a] These figures divided by 100 represent the ratios of diolefin to isobutylene units in the polymer.

These figures are accurate to about 10 per cent.

It was necessary to include two or more polymers of about the same unsaturation value but differing in average molecular weight to obtain sufficiently large fractions covering the desired range of molecular weights. Selection of polymers of exactly the same molecular weight was not feasible, owing to the fact that the more accurate ozonolysis method was not established until much of the experimental work had been completed. However, except for minor variations, the polymers which had been selected fell into two classifications. The first includes polymers I, II, and III (Table I) which contained about 0.5 mole-per cent of diolefin units; those of the second group, consisting of polymers IV and V, possessed slightly over 1.0 mole-per cent of diolefin. These will be referred to merely as the low- and high-unsaturation polymers, respectively. These terms are relative; the so-called high-unsaturation polymers contained only a little over 1 per cent of the unsaturation occurring in natural rubber and most of the other synthetics.

Molecular Weights of Fractions.—The fractions employed in this investigation are listed in Table II. The Roman numerals included with the identifying designation in the first column refer to the raw polymer (Table I) from which the fraction was prepared. The fractions from a given raw polymer are arranged approximately in the order of decreasing molecular weight. The second column shows the proportions of precipitant (acetone) used in separating the fraction from preceding and succeeding fractions. For example, polymer I-2 was obtained by precipitating with 3.5 cc. of acetone per 100 cc. of benzene, the preceding fraction having been removed by 3.0 cc. of acetone per 100 cc. of benzene.

Owing to faulty compounding and curing procedures in the preliminary stages of the investigation, much fractionated polymer was wasted in the

TABLE II

MOLECULAR WEIGHTS OF FRACTIONS

Polymer fraction designation	Precipitant range	Percentage of original polymer in fraction	Intrinsic viscosity [η]	$M \times 10^{-3}$	After compounding (pure-gum recipe)[a]	
					[η]	$M \times 10^{-3}$
I-1	2.5 – 3	6.9	2.80	1200	2.63	1080
I-2	3 – 3.5	7.4	2.30	875	2.05	730
I-3	2.5 – 3.25	36.3	2.18	805	1.98	690
I-4	3.25– 4	12.3	2.02	715	1.90	650
I-5	3.5 – 4	15.2	1.98	690	1.72	555
I-6	3.75– 4.5	..	1.77	580	..	..
II-1	4 – 4.5	..	1.87	635	..	..
II-2	4.5 – 5	18.4	1.41	410	1.37	390
II-3	5 – 5.5	10.7	1.19	310	1.19	310
II-4	5 – 5.5	13.0	1.27	345	1.12	285
II-5	5.5 – 6	8.7	1.12	285	1.02	245
II-6	5 – 6	22.9	1.12	285	..	..
II-7	6 – 7	9.8	0.89	200	0.90	202
II-8	6 – 7.5	18.5	0.81	172	0.81	172
II-9	7 – 8.5	14.2	0.75	152	0.75	152
II-10	7 – 8.5	12.0	0.72	143	0.75	152
II-11	8.5 –11	..	0.67	127	..	..
II-12	8.5 –11	6.4	0.61	110	0.61	110
II-13	8.5 –11	5.5	0.60	108	0.60	108
III-1	5 – 6	17.0	..	..	1.02	245
III-2	5 – 6	10.5	1.07	265	..	..
III-3	6 – 7	4.0	0.93	213	0.92	210
III-4	6 – 7	13.1	0.85	185	..	(185)
III-5	6 – 7.5	28.8	0.80	168	..	..
III-6	7 – 8	19.6	0.73	146	0.72	143
III-7	7.5 –10	19.3	0.63	116	..	..
III-8	8 –10	16.3	0.58	102	0.60	108
III-9	10 –12	5.1	0.55	94	..	..
III-10	10 –12	15.9	0.515	85	0.515	85
III-11	10 –12	10.3	0.50	81	..	(81)
III-12	12 –15	13.5	0.40	57	..	..
III-13	12 –15	5.4	0.42	62	..	(62)
III-14	15 –20	9.5	0.36	48.5	..	(48.5)
III-15	15 –20	5.6	0.33	42.5	..	..
III-16	20 –30	5.7	0.284	33.5	..	(33.5)
III-17	20 –30	..	0.265	30.0	..	..
III-18	25 –35	4.0	0.24	25.8	..	..
III-19	30 –50	..	0.186	17.3	..	(17.3)
IV-1	5 – 6	13.6	1.20	410	1.23	330
IV-2	6 – 7	20.6	0.98	230	1.04	250
IV-3	7 – 8	10.5	0.79	165	0.82	175
IV-4	8 –10	..	..	..	0.67	127
IV-5	9 –10	6.0	0.66	125	0.65	122
IV-6	12 –15	10.0	0.43	64	..	(64)
IV-7	15 –20	6.0	0.35	46.5	..	(46.5)
IV-8	20 –30	7.0	0.258	28.8	..	..
IV-9	30 –50	3.5	0.185	17.1	..	..
V-1	0 – 5	18.6	1.85	620	1.77	580
V-2	5 – 5.5	15.0	1.57	480	1.57	480
V-3	5.5 – 6	6.2	1.36	385	1.40	400
V-4	6 – 7	11.1	1.09	270	1.11	280
V-5	7 – 8	5.2	0.99	235	1.02	245
V-6	8 –10	18.8	0.76	155	..	(155)
V-7	12 –15	5.5	0.41	60	..	(60)
V-8	15 –20	3.8	0.36	48.5	..	(48.5)

[a] Since the lower fractions undergo no appreciable breakdown during compounding, their viscosities after mixing usually were not determined. Wherever the compounded (uncured) molecular weight has been assumed in the discussion to be the same as the molecular weight before mixing, that molecular weight is included in parentheses in the last column.

preparation of vulcanizates which had to be discarded. Consequently in most cases two or more batches of the same raw polymer were fractionated, which explains the overlapping and duplicate fractions from the same polymer (Table II). Two fractions obtained between the same precipitant range are not, of course, identical, owing to the slight irreproducibility of fractionation.

A few of the fractions contained a larger percentage (column 3, Table II) of the raw polymer than was intended. The somewhat broader molecular weight distribution in these fractions, most of which were of high molecular weight, is not believed to have introduced noteworthy errors into the results.

The molecular weights of the fractions (column 5) were calculated from their intrinsic viscosities in diisobutylene, measured as described above and in reference[7], using the equation:

$$\log M = 5.378 + 1.56 \log [\eta] \tag{1}$$

This equation, previously established for polyisobutylene[7], was found to be equally applicable to Butyl polymers[11], as would be expected.

The polymer fractions were by no means strictly homogeneous. They are believed to have been sufficiently so, however, that the various average molecular weights differed only slightly. These differences between the averages should not be totally disregarded, and for this reason a brief discussion is included of the interrelation of different average molecular weights.

The number, weight, and viscosity average molecular weights are defined, respectively, as follows:

$$\overline{M}_n = \sum_i N_i M_i / \sum_i N_i \tag{2}$$

$$\overline{M}_w = \sum_i N_i M_i^2 / \sum_i N_i M_i \tag{3}$$

$$\overline{M}_v = [\sum_i N_i M_i^{a+1} / \sum_i N_i M_i]^{1/a} \tag{4}$$

where N_i is the number of molecules of molecular weight M_i, and the summations extend over all species in the mixture. The quantity a in the formula for the viscosity average molecular weight[7] is the exponent in the alternate form of the intrinsic viscosity-molecular weight formula 1:

$$[\eta] = K\overline{M}_v^a \tag{1A}$$

That is, $a = 1/1.56 = 0.64$ for polyisobutylene or Butyl rubber in diisobutylene. For a heterogeneous polymer $\overline{M}_w$ necessarily exceeds $\overline{M}_n$; their ratio is greater than unity by an amount dependent upon the breadth of the molecular weight distribution. For this value of a, $\overline{M}_v$ lies between $\overline{M}_n$ and $\overline{M}_w$, but much nearer the latter. The intrinsic viscosity relates directly to this average, regardless of molecular weight distribution.

Equation 1 is based on an empirical comparison[7] of the intrinsic viscosities (in diisobutylene) of fractions which were prepared essentially as were those of Table II with their absolute number-average molecular weights determined by the osmotic pressure method. Since the degree of heterogeneity in the fractions employed here was therefore similar to those used in establishing Equation 1, it is clear that the M values in column 5, Table II, represent number averages of the relatively homogeneous fractions to a good approximation.

According to the theory of fractionation, in so far as it has been developed, we estimate that the heterogeneity of the fractions was such that $\overline{M}_w$ in general

exceeds $\overline{M}_n$ by some 10 to 15 per cent; the viscosity-average molecular weights of the fractions probably run about 10 per cent higher than the M values in column 5 of Table II. Likewise, when Equation 1 is applied to unfractionated polymers, the average molecular weight obtained is about 10 per cent below the true viscosity average ($\overline{M}_n$ being half or less of $\overline{M}_v$, depending on the heterogeneity). The molecular weights for the unfractionated polymers of Table I have not been corrected by this rather uncertain factor; hence, they are lower than the true viscosity averages by some 10 per cent.

When the higher fractions were compounded on the mill, some breakdown inevitably occurred in spite of the precautions discussed in the preceding section. The degree of degradation was not large, however. This is shown by the intrinsic viscosities of the fractions after compounding (column 6, Table II), which were determined by dissolving weighed samples of the compounded rubber (pure-gum recipe) in diisobutylene, correction being made for the weight of compounding ingredients. Independent experiments established that these did not alter the viscosity.

In the degradation of polymers under the influence of mechanical working of this sort it is known that larger species are degraded preferentially. In consideration of this fact and the relatively small changes which occurred, it is unlikely that the heterogeneity was appreciably increased by milling. The molecular weights based on intrinsic viscosities of the compounded rubbers undoubtedly approximate number averages closely, in so far as heterogeneity is a factor in the samples.

Fractions of lower molecular weight survive milling without measurable degradation. For this reason intrinsic viscosities of many of the low-molecular-weight fractions were not redetermined after compounding. Some of the high-unsaturation fractions intermediate in molecular weight showed increases in intrinsic viscosity after compounding. The onset of the vulcanization reaction to a minute extent during milling may have been responsible for this change, which in any event was too small to warrant further consideration.

Diolefin Content of Individual Fractions.—Rehner[12] showed that the isoprene units in Butyl rubber are distributed more or less at random along the polymer chains. From this fact and the nature of the polymerization process it is to be expected that the proportion of diolefin units in high and in low-molecular-weight fractions from the same raw polymer should be very nearly the same. To confirm this expectation, the percentage unsaturation in several of the fractions was measured by the ozonolysis method[10].

This method is based on the knowledge that all, or nearly all, of the isoprene units occur in the 1,4-configuration within the main chain[12]. When the solution of polymer in carbon tetrachloride is ozonized, these units are split. As Rehner showed, the degradation proceeds to a limit corresponding to complete reaction of the diolefin units, beyond which further ozonization produces little change. The percentage of diolefin units, consequently, is proportional to the increase in the number of molecules during ozonization. Specifically:

$$\text{mole-per cent diolefin} = (1/\overline{M}_n - 1/\overline{M}_{n,0}) \times 56 \times 100$$

$\overline{M}_{n,0}$ and $\overline{M}_n$ are the number-average molecular weights before and after ozonization, and 56 is the molecular weight per structural unit, the diolefin units being present in extreme minority.

Table III gives typical experimental results on Butyl fractions. $\overline{M}_{n,0}$ is equal to M of Table II, calculated from the initial intrinsic viscosity of the fraction. The molecular weights in the fifth column of Table III were com-

TABLE III

PERCENTAGE UNSATURATION DISTRIBUTION AMONG POLYMER FRACTIONS

Polymer fraction	Before ozonolysis		After ozonolysis			Mole-per cent diolefin
	$M \times 10^{-3}$	$10^4/M$	$[\eta]$	"M_v" $\times 10^{-3}$	$10^4/M_n$	
II-4	345	2.9	0.179	16.3[b]	102	0.56
II-5	285	3.5	0.181	16.6[b]	100	0.54
II-7	200	5.0	0.182	16.8[b]	99	0.53
II-11	127	7.9	0.179	16.4[b]	101	0.52
III(0–5)[a]	370	2.7	0.191	18.1[b]	92	0.50
III-6	146	6.8	0.195	18.7[b]	89	0.46
III-12	57	17.6	0.179	16.4[b]	101	0.47
III-16	33.5	29.9	0.165	15.5[b]	115	0.48

[a] This sample, representing a first fraction from a fractionation of polymer III, is not included in Table II.

[b] The absolute viscosity-average molecular weights are slightly larger than the figures given in this column (see text).

puted from the intrinsic viscosity after ozonization using Equation 1. In accordance with the previous discussion, it is somewhat less than the actual viscosity-average molecular weight. Owing to the (assumed) random distribution of diolefin units in the samples and the fact that, in general, each molecule is split at a number of points, the distribution of molecular weights in the ozonized products will approximate the most probable distribution[13], represented by equation:

$$N_i = Np^{i-1}(1 - p) \tag{5}$$

where N_i = number of molecules composed of i structural units
N = total number of molecules
$1 - p$ = degree of degradation or ratio of molecules to structural units in the sample

$$\overline{M}_n = 1/(1 - p) \tag{6}$$

When Equation 5 is substituted into Equation 4, it is found that for this molecular weight distribution:

$$\overline{M}_v/\overline{M}_n = 1.83$$

(The derivation of this factor was published by Rehner[10].) Allowing that the actual viscosity-average molecular weights are about 10 per cent greater than the uncorrected values in column 5 of Table III:

$$\overline{M}_n = \text{"}\overline{M}_v\text{"}/1.66$$

By means of this equation the reciprocal $\overline{M}_n$ values in column 6 were computed. The diolefin percentages in the last column were calculated from columns 6 and 3 by the above equation. The variations in these percentages are probably within the experimental error, and there is no significant trend with molecular weight. It is the constancy of the diolefin content, rather than its absolute magnitude, that is of importance for interpretation of the results which follow.

Mixtures of Fractions.—All rubbers, natural and synthetic, as normally employed are composed of molecular species covering a wide range of sizes. It is important, therefore, to ascertain the effects of molecular-weight distribution on various physical properties. For this purpose heterogeneous polymers of known distribution were required. These were conveniently obtained by mixing pairs of fractions in various proportions as shown in Table IV. Data

TABLE IV

MIXTURES OF FRACTIONS

Mixt. designation	Percentage of polymer of lower mol. wt.	$[\eta]$ calcd.[a]	$[\eta]$ observed after compounding	$M_n \times 10^{-3}$ calcd.[b]	"M_v" $\times 10^{-3}$ calcd. from $[\eta]$ after compounding	M_w calcd.[b]
I-3	0	(2.18)	1.98	805	690	805
A-1	10	2.01	1.92	435	660	735
A-2	20	1.84	1.76	300	575	660
A-3	40	1.51	1.43	183	415	520
A-4	65	1.09	1.02	124	245	335
III-10	100	(0.515)	0.515	85	85	85
			Series B			
II-2	0	(1.41)	1.37	410	390	410
B-1	25	1.24	1.24	280	335	345
B-2	50	1.605	1.07	210	265	275
B-3	75	0.89	0.86	171	188	210
II-10	100	(0.72)	0.75	143	152	143
			Series C			
II-1	0	(1.87)	..	635	..	635
C-1	10	1.71	1.53	210	465	575
C-2	20	1.55	..	126	..	515
C-3	35	1.31	1.31	79	365	420
III-17	100	(0.265)	..	30	30	30
			Series D			
I-6	0	(1.77)	..	580	..	580
D-1	40	1.32	1.21	240	320	400
D-2	65	1.05	1.03	175	250	285
II-11	100	(0.67)	..	127	..	127

[a] Observed intrinsic viscosities of uncompounded individual fractions shown in parentheses; intrinsic viscosities of their mixtures calculated from Equation 5.

[b] Number- and weight-average molecular weights calculated from molecular weights of individual fractions before compounding.

pertaining to the individual fractions from which each series of mixtures was prepared are included with each set; these are taken from Table II. Intrinsic viscosities in the third column have been calculated for the mixtures by "weight averaging" according to the formula:

$$[\eta]_{mixture} = w_1[\eta]_1 + w_2[\eta]_2 \qquad (7)$$

where w_1 and w_2 are the weight fractions of the components present in the mixture, and $[\eta]_1$ and $[\eta]_2$ are their respective intrinsic viscosities (uncompounded). The observed intrinsic viscosities after compounding (column 4) are generally somewhat lower, owing to a small degree of breakdown during milling.

The effects of molecular weight heterogeneity on a given physical property—*e.g.*, on tensile strength—are easily accountable if it can be shown that the property in question depends explicitly on a particular average molecular weight but is otherwise independent of the distribution. A plot of the physical property against this average molecular weight will be the same for various heterogeneous polymers and for homogeneous fractions as well[14]. Once the specified average has been evaluated for a given polymer, no further consideration need be given the molecular weight heterogeneity. It is not self-evident in advance of experimental verification, however, that an average can be found such that the property in question is specifically defined by the value of that average alone.

In the analysis of the data on physical properties of vulcanizates from fractions and their mixtures, the number, weight, and viscosity averages defined by Equations 2, 3, and 4, respectively, were considered. The first two may be computed from the following expressions applicable to binary mixtures:

$$\overline{M}_n = 1/(w_1/M_1 + w_2/M_2) \tag{2A}$$

$$\overline{M}_w = w_1M_1 + w_2M_2 \tag{3A}$$

which follow from Equations 2 and 3; w_1 and w_2 are the weight fractions, and M_1 and M_2 are the molecular weights of the component polymer fractions. In computing $\overline{M}_n$, M_1 and M_2 should refer to the number averages for the component fractions; in computing $\overline{M}_w$, weight averages should be employed in so far as the heterogeneity of the fractions is to be taken into account.

The number-average molecular weights in column 5 of Table IV were computed using Equation 2 from the M values for the individual fractions before compounding, as given in Table II; as pointed out above, the latter correspond more closely to number averages. Some breakdown generally occurred during compounding, but undoubtedly only the large component fraction was affected. Minor degradation of these would lower the number averages for the mixtures negligibly. Hence, the $\overline{M}_n$ values for the mixtures in Table IV should correspond closely to their actual number-average molecular weights.

In the computation of the weight averages (Table IV), the M_1 and M_2 values inserted into formula 3A should have been increased by about 10 to 15 per cent, according to the estimate quoted above, owing to the residual heterogeneity of the fractions. If this correction were made, assuming all fractions to be equally heterogeneous, the figures in the last column of Table IV would be raised somewhat, but all of them by about the same percentage. Since mixtures and fractions would be equally affected by this correction, any possible empirical correlation of a physical property with the weight average would not be obscured through the use of the uncorrected figures for $\overline{M}_w$ in Table IV.

This average molecular weight, unlike $\overline{M}_n$, is sensitive to the destruction of the larger species during mill breakdown, which occurs to an extent depending on the percentage of low-molecular-weight fraction in the mixture. A more nearly authentic weight average perhaps would be obtained by assuming that the breakdown which occurs is confined to the higher of the two components. However, more accurate values for the weight-average molecular weights are not required for the purposes of the subsequent discussion of physical properties, and this correction has been neglected.

The uncorrected viscosity-average molecular weight, calculated using Equation 1 from intrinsic viscosities after compounding, are also included in Table IV.

In addition to the heterogeneous products obtained by mixing fractions, polymer II–A of Table I was compounded without previous fractionation, and the resulting vulcanizates were subjected to tests. Its molecular weight distribution was determined by careful fractionation on a small scale. According to an analysis of its distribution curve, the ratio of $\overline{M}_v/\overline{M}_n$ was found to be about 2.3 ± 0.2. Its corrected viscosity-average molecular weight should be about 470,000. Hence, $\overline{M}_n = 200{,}000$. This value will be employed in subsequent discussions.

STRUCTURE OF BUTYL VULCANIZATES

Theory.—The process of cross-linking polymer molecules has been analyzed statistically[2], with results which are confirmed by widespread experimental observations. As cross-linkages are introduced at random between polymeric molecules at accidental points of contact, large structures consisting of many "primary molecules" gradually are built up at the expense of simple molecules consisting of only one primary molecule (not cross linked), or of only a few primary molecules. (The term "primary molecule" throughout this paper refers to the rubber molecules which existed separately before cross-linking, or which would exist if all of the cross-linkages of the vulcanizate were severed.) According to the statistical theory, "infinite" networks pervading the entire rubber volume suddenly begin to form, owing to interlinking of these large species, when the concentration of cross-linkages in the system as a whole exceeds a definite critical limit. If the primary molecules are of uniform length, this occurs when the number of cross-linkages exceeds half the number of primary molecules[15]; if the molecules are nonuniform in length, a somewhat lower degree of cross linking will be required[2]. These infinite networks are insoluble in all solvents which do not destroy their primary valence structure. Their abrupt appearance at an early stage of the vulcanization process is analogous to the gel point so familiar in the polymerization of thermosetting resins, drying of oils, etc.

As the vulcanization process continues, introduction of additional cross-linkages causes more and more of the sol rubber to be converted to gel (infinite networks). Ordinarily the final vulcanizate will consist almost entirely of gel, which is a statistical consequence of the fact that there are, on an average, many cross-linked units per primary molecule.

From a structural point of view, the individual primary molecules to a large extent have lost their identities in the final vulcanizate. The basic element of the structure (Figure 2) is the portion of a molecule reaching from

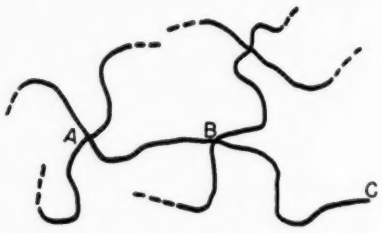


Fig. 2.—Diagrammatic representation of a portion of the network structure, showing principal chains *AB* and a terminal chain *BC*.

one cross-linkage to the next—*e.g.*, the portion of the structure between the cross-linkages designated by *A* and *B*. This primary structural element will be referred to as a chain. The cross-linkages may be regarded as centers of tetrafunctionality since four chains emanate from each. The network consists of an assemblage of chains attached irregularly to one another through these tetrafunctional centers[16].

In addition to chains extending between two cross-linkages, there will be chains extending from a cross-linkage to the end of a primary molecule; two of these "terminal" chains will occur in the network for each primary molecule. It is apparent that these terminal chains, unlike the principal chains, will not be

subjected to permanent orientation when the network is deformed as by stretching. The terminal chains constitute flaws in the network structure. The lower the molecular weight (number average) of the primary molecules, the greater the number of these flaws. Hence, the well known but poorly understood dependence of physical properties on the molecular weight of the uncured rubber[17].

The total number of chains is equal to $\nu_0 + N$, where ν_0 is the number of cross-linked units (the number of cross-linkages being equal to $\nu_0/2$), and N is the number of primary molecules in the network. The concentration of primary molecules, expressed in moles per gram, is related to the molecular weight of the primary molecules as follows:

$$N/\rho V = 1/M$$

where ρ is the density and V the volume containing N primary molecules. For a heterogeneous mixture M should be replaced by the number average, $\overline{M}_n$. Similarly, the concentration of cross-linked units is given by:

$$\nu_c/\rho V = 1/M_c$$

where M_c is the molecular weight (number average) per cross-linked unit; it will be used extensively as a reciprocal measure of the concentration of cross-linked units.

It follows, then, that the total concentration of chains, in moles per gram, equals $1/M_c + 1/M$. The molecular weight (number average) per chain, designated by M_c', equals the reciprocal of this quantity:

$$M_c' = MM_c/(M + M_c) \tag{8}$$

When $M > > M_c$:

$$M_c' \cong M_c \tag{8A}$$

Inasmuch as the diolefin units are distributed at random along the polymer chains and vulcanization can safely be assumed to interlink them at random, the lengths of the chains conform to the most probable distribution expressed by Equation 5. Furthermore, terminal chains and principal network chains have the same average size. The weight fraction of the network occurring in terminal chains, therefore, equals the "mole" fraction of terminal chains. Since there are two terminal chains for each primary molecule, the percentage of nonorienting material in the network structure is given by:

$$\begin{aligned} \text{per cent terminal chains} &= 100 \times (2/M)/(1/M_c') \\ &= 100 \times 2M_c/(M + M_c) \end{aligned} \tag{9}$$

When $M > > M_c$:

$$\text{per cent terminal chains} \cong 100 \times (2M_c/M) \tag{9A}$$

These relationships will be applied in the subsequent treatments of physical properties.

Quantitative Evaluation of Degree of Cross-Linking.—The preceding discussion makes it clear that the two quantities essential to the quantitative treatment of vulcanizate properties are M and M_c. The former has been determined (Table II) through the application of accepted methods for molecular weight determination. Direct chemical determination of M_c by chemical measurement of the concentration of cross-linkages in rubber vulcanizates has not yet proved feasible. Therefore this quantity has been deduced indirectly by locating the critical point for incipient gelation in the manner described below.

It has been assumed that the reactivities of the diolefin units are independent of polymer molecular weight, location of diolefin unit within the polymer molecule, etc. Under this assumption, substantiated by numerous observations on the kinetics of polymer reactions, all polymers of the same diolefin content acquire the same concentration, *e.g.*, in moles per liter, of cross-linkages during the vulcanization process, regardless of the molecular weight of the initial polymers; hence, the average number of cross-linkages per primary molecule varies inversely as the initial molecular weight. According to the statistical theory of three-dimensional polymers, infinite network formation sets in, with attendant partial insolubility, when an average of one unit per primary molecule (one-half cross-linkage per molecule) is present[15]. Hence, a "vulcanizate" which borders on incipient insolubility must contain an average of one cross-linked unit per primary molecule. In other words, at the critical point for incipient gelation $M_c = M$, where M is the molecular weight of the polymer prior to cross-linking. This polymer is here considered to be homogeneous. (If the polymer is heterogeneous, then $M_c = \overline{M}_w$ at the critical point[18]. Once the critical M, and hence M_c, is located, it follows from the above assumption that this M_c value applies to all vulcanizates from fractions containing the same proportion of diolefin units, regardless of molecular weight.

Table V lists experimental results for low-molecular-weight fractions compounded according to the pure gum recipe and subjected to "cure" at 307° F. All fractions within each set are assumed to possess the same proportion of diolefin units, according to the results previously presented. As the molecular

TABLE V

INCIPIENT CURE WITH BUTYL FRACTIONS OF LOW MOLECULAR WEIGHT

Polymer fraction	Intrinsic viscosity[a] $[\eta]$	$M \times 10^{-3}$	Time of cure (min. at 307° F)	Per cent soluble	Swelling ratio[b]	$[\eta]$ after curing process
Fractions from low-unsatn. polymers II and III						
III-6	0.72	143	60	1.6	10.8	..
II-12	0.61	110	60	6.5	11.4	..
III-10	0.515	85	60	10.5	14.6	..
III-13	0.42	62	60	24.6	29.2	..
			120	29.3	35.8	..
III-14	0.36	48.5	30	40	40	..
			60	35	41	..
			120	49	53	..
III-16	0.284	33.5	60	100	..	0.43
			120	100	..	0.34
III-19	0.186	17.3	120	100	..	0.24
Fractions from high-unsatn. polymer IV						
IV-5	0.65	122	40	2.3	..	..
IV-6	0.43	64	40	4.4	..	..
IV-7	0.35	46.5	40	12.6	..	..
			80	13.8	..	..
IV-8	0.258	28.8	40	50	..	..
			80	75	..	..
IV-9	0.185	17.1	40	100	..	0.211
			80	100	..	..

[a] On these low-molecular-weight fractions the intrinsic viscosity is not altered appreciably by milling. In cases where $[\eta]$ has been measured both before and after milling, the latter value has been employed above (Table II).

[b] Swelling ratio = [vol. of swollen vulcanizate] / [vol. of insol. rubber (dry)]. Swelling and solubility determinations were carried out in cyclohexane at room temperature.

weight was decreased, the percentage of sol (soluble constituents) increased from about 1 per cent or less for fractions of high or medium molecular weight, to complete solubility for the lowest fractions. The latter, which were too low to contain the critical number of cross-linkages per molecule required for gelation, nevertheless underwent an increase in intrinsic viscosity as a result of the cross-linking reaction (last column, Table V). Swelling ratios for the gels are also included in Table V.

The molecular weight differences between successive fractions are necessarily rather large. From casual examination of the data, the M_c values can be bracketed only between rather wide limits—33,500 to 48,500 for the low-unsaturation polymers and 17,000 to 28,800 for those of high unsaturation. Further assistance is afforded by the theory of random cross-linking[15] of chains of uniform length in the form of the equation:

$$(-\ln W_s)/(1 - W_s) = \gamma \tag{10}$$

relating the weight fraction of sol W_s to the "cross-linking index", γ; the latter represents the average number of cross-linked units per primary polymer molecule. In other words:

$$\gamma = M/M_c$$

where M is the molecular weight of the fraction. By arbitrarily choosing M_c values within the required limits, trial sets of γ values are obtained from the known molecular weights of the fractions. These can be compared graphically, as in Figure 3, with the curve calculated from Equation 10. M_c values of

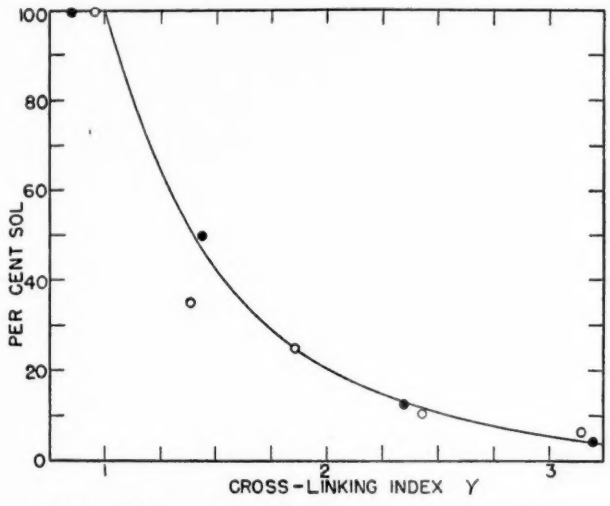


FIG. 3.—Weight per cent of sol (100 × W_s) *vs.* cross-linking index. Assuming M_c = 35,000 for low-unsaturation polymers ○, and M_c = 20,000 for high-unsaturation polymer IV fractions ●; (i.e., $\gamma = M/M_c$).

35,000 and 20,000, respectively, appear to give the best fit with the calculated curve. These values were employed in obtaining the sets of points shown in Figure 3. The agreement is reasonably good and, to some extent, confirms the present concepts of the nature of the vulcanization process. This method of evaluation is essentially a graphical extrapolation to the molecular weight

at which the solubility reaches 100 per cent, guided by the form of the theoretically prescribed relationship.

The above figures for M_c will be employed in the following discussion of physical properties. Their reciprocals, 2.85×10^{-5} and 5.0×10^{-5} "mole" per gram, respectively, represent the concentrations of cross-linked units in vulcanizates from the low- and high-unsaturation polymers; concentrations of cross-linkages are half of these values.

Discussion.—In deducing the values for M_c, it has been assumed that the interconnections between molecules are simple cross-linkages between two molecules. If three or more molecules were united at the junctions formed during vulcanization, the above procedure would require revision; the critical molecular M would then be less than M_c, the molecular weight per cross-linked unit, by a factor depending on the (average) functionality of the intermolecular linkages. Owing to the low concentration of diolefin units available to the action of the vulcanizing ingredients, it is most unlikely that more than two of them would be linked together, irrespective of the actual nature of the vulcanization reaction. This inference is supported by independent confirmation of the M_c values, obtained in the analysis of the dependences of "modulus" and swelling capacity on molecular weight (to be discussed later in the paper). This agreement would not be observed if the intermolecular connections were of higher functionality.

A 35,000 molecular weight portion of one of the low-unsaturation Butyl polymers includes an average of 3.1 diolefin units, from which we conclude that only about 1 diolefin unit in 3 enters into the formation of cross-linkages. Similarly, the 20,000 figure for the molecular weight between cross-linkages in polymer IV corresponds to the somewhat lower cross-linking efficiency of 1 in about 3.7. In other experiments not reported here, gelation conditions were explored by varying the degree of unsaturation at constant molecular weight. At a molecular weight level of 350,000, between 0.075 and 0.12 mole-percentage of diolefin units are required for incipient gelation during vulcanization, using the standard recipe. At a molecular weight level of 900,000, a mole percentage of diolefin units between 0.016 and 0.030 is required. These figures represent from 3 to 5 diolefin units per molecule in each case. Thus, the efficiency of utilization of diolefin units in the formation of cross-linkages shows a remarkably small variation over a 100 fold range of diolefin concentration.

Doubling the proportions of the compounding ingredients lowers the molecular weight for incipient gelation during vulcanization, as would be expected from results presented in connection with the description of experimental procedures. In the case of fractions from Butyl polymer IV the critical molecular weight (equal to M_c) is lowered to about 15,000. Hence, it is possible to increase the efficiency of utilization of the diolefin units through the use of a greater concentration of compounding ingredients.

By employing nonsulfur vulcanizing agents, it is possible to produce gelation with less than 2 (but more than 1) diolefin units per molecule. Even at molecular weights in the vicinity of 1,000,000, no more than 1 diolefin unit in 10,000 is required for incipient network formation. Polymers containing no diolefin units (i.e., pure polyisobutylene) yield completely soluble products when subjected to the same curing conditions.

In this connection, sulfur-accelerator vulcanization of mixtures of polyisobutylene and Butyl yields products from which the polyisobutylene can be removed by extraction. This result provides direct proof that the cross-linkages involve 2 diolefin units, and not a diolefin unit in one molecule with an isobutylene unit in the other.

STRESS–STRAIN CHARACTERISTICS

Figure 4 shows stress-strain curves covering the range 0 to 500 per cent elongation, for representative pure-gum vulcanized Butyl fractions differing in molecular weight and in unsaturation.

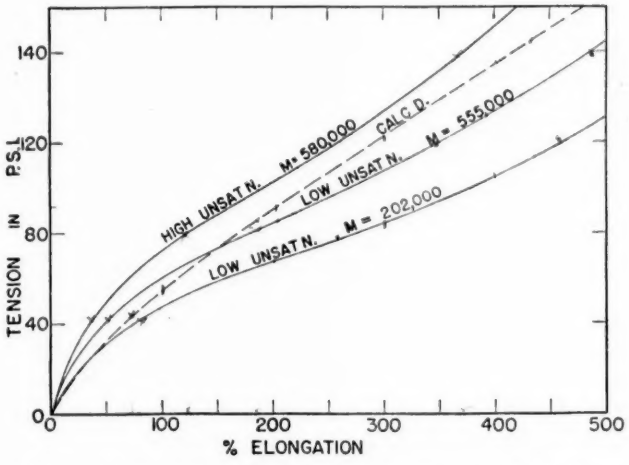


Fig. 3.

FIG. 4.—Representative stress-strain curves for pure-gum vulcanizates at moderate elongations.

In Figure 5 stress-strain curves extending over virtually the entire elongation region and extending to stresses of 700 pounds per square inch are shown for a series of low-unsaturation Butyl fractions vulcanized according to the pure gum recipe previously given. These cover the molecular weight range 110,000 to 730,000. Progressive changes with molecular weight are particularly great in the region of low molecular weight. They continue, however,

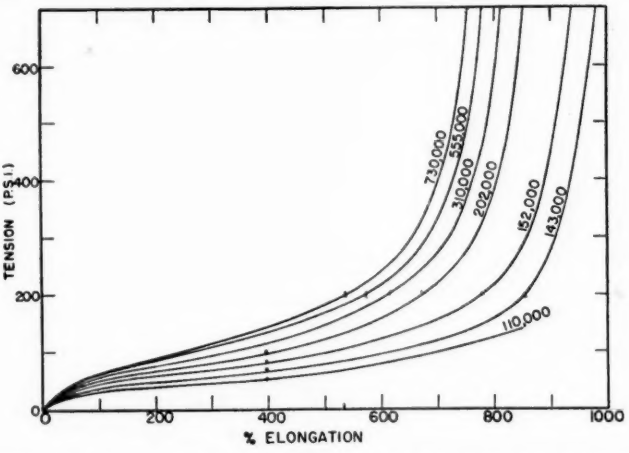


Fig. 4.

FIG. 5.—Stress-strain curves extending to high elongations for vulcanizates from low-unsaturation fractions of the molecular weights indicated.

even above a molecular weight of 500,000, where there is an average of some fourteen cross-linked units per molecule according to our previous estimate of M_c.

Stress-Strain Curves at Moderate Elongations.—Careful analysis of stress-strain curves, including others not shown here, reveals a common similarity in shape. If each is transformed simply by altering its tension scale by a suitable factor, all of them may be made to coincide as far as about 400 per cent elongation. Some deviations occur with the vulcanizates from the fractions of low molecular weight, possibly as a result of high hysteresis. In all other cases, including stress-strain curves for high-unsaturation vulcanizates and vulcanizates from unfractionated polymers, the coincidence is excellent. In other words, essentially all of the stress-strain curves from 0 to 400 per cent elongation can be represented by:

$$\tau = G\varphi(\alpha) \tag{11}$$

τ is the tension, in pounds per square inch (initial cross-section) at a relative length $\alpha = L/L_0$ [per cent elongation = $100 \times (\alpha - 1)$]; $\gamma(\alpha)$ is a function of α which is the same for all of the pure-gum Bütyl vulcanizates. G is a parameter which varies from one sample to another; G is dependent on the molecular weight before vulcanization and on the number of cross-linkages introduced during vulcanization, but is independent of α.

The separability of structure (G) and elongation [$\varphi(\alpha)$] factors as in Equation 11 is predicted by statistical mechanical theories of the elastic properties of network structures such as exist in vulcanized rubbers. According to these theories[19], the dependence of the elastic retractive force on elongation should be represented by:

$$\varphi(\alpha) = \alpha - 1/\alpha^2 \tag{12}$$

This expression can be expected to apply only over the elongation region preceding the onset of crystallization. It is further assumed in its derivation that the force of retraction originates entirely from the entropy change on stretching, the change in internal energy with elongation (at constant volume) being negligible. The latter condition is amply fulfilled with natural rubber[20] and GR-S[21].

In Figure 4 a stress-strain curve calculated from Equation 12 is included for comparison with the shape of the observed curves over the region of moderate elongations—*i.e.*, up to 400 per cent. The agreement is by no means so good as has been demonstrated for natural rubber[22] and GR-S[21]. However, the curves observed here, being determined by continuous stretching, are not necessarily representative of the equilibrium curve to which Equation 12 refers. This may account for a large part of the discrepancy. We are less concerned with the particular shape of the stress-strain curve than with the dependence of stress on structure.

In view of the empirically established separability of the structure and elongation factors as expressed in Equation 11, the stress-strain curve for a given Butyl vulcanizate (pure-gum cure) can be characterized by a single parameter. Either G or the tension at a given elongation might be used for this purpose. We have chosen to employ the tension developed at 300 per cent elongation. These so-called moduli at 300 per cent elongation, as taken from the stress-strain curves for various samples, are recorded in Tables VI and VII. They are shown graphically as functions of the molecular weight before vulcanization in Figure 6.

TABLE VI

STRESS-STRAIN AND SWELLING CHARACTERISTICS OF LOW-UNSATURATION BUTYL VULCANIZATES
(Cured 60 minutes at 307° F)

Polymer fraction or mixt.[a]	$M \times 10^{-3}$ (after compounding)	τ_{300}%[b], (lb. per sq. in.)	Percentage elongation at 500 lb. per sq. in.	Per cent soluble	Swelling ratio[c]
Vulcanizates from homogeneous fractions					
I-1	1080	..	..	0	6.13
I-2	730	116	730	0	6.30
I-5	555	108	755	0	6.70
II-3	310	94	790	1.0	7.18
II-5	245	..	..	0.5	7.52
II-7	202	84	825	0.9	7.90
II-9	152	68	905	1.0	9.53
III-6	143	55	955	1.6	10.8
II-12	110	45	..	6.5	11.35
III-10	85	..	..	10.5	14.6
Vulcanizates from heterogeneous polymers[d]					
A-1	435	..	..	2.6	6.82
A-2	300	..	..	3.2	7.38
A-3	183	..	..	4.5	8.22
A-4	124	..	..	7.5	10.35
D-2	175	..	..	..	..
II-A	200	78	865	3.5	8.05

[a] See Tables II and IV.
[b] "Modulus" at 300 per cent elongation.
[c] Swelling measurements were carried out in cyclohexane on ring specimens cured simultaneously with those used for stress-strain measurements.
[d] Molecular weights for these mixtures are number averages (Table IV).

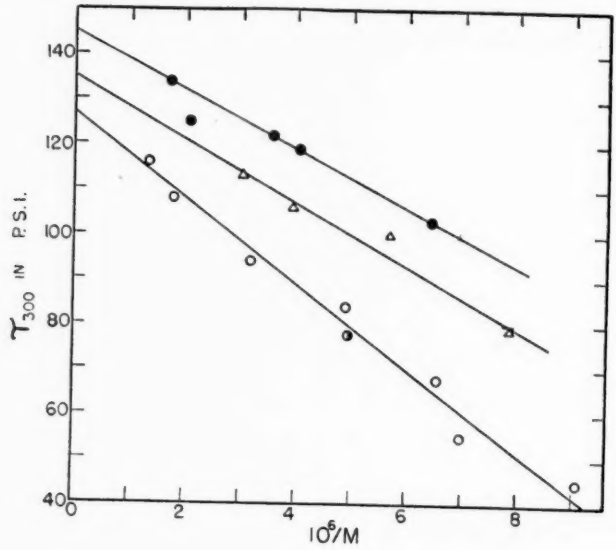
TABLE VII

STRESS-STRAIN AND SWELLING CHARACTERISTICS OF HIGH-UNSATURATION BUTYL VULCANIZATES

Polymer fraction	$M \times 10^{-3}$ (after compounding)	Cure (min. at 307° F)	τ_{300}%, (lb. per sq. in.)	Percentage elongation at 500 lb. per sq. in.	Swelling ratio[a]
IV-1	330	40	113	700	6.46
IV-2	250	40	106	725	6.57
IV-3	175	40	100	720	7.13
IV-4	127	40	79	..	8.30
IV-5	122	40	..	..	7.94
IV-6	64	40	..	..	11.0
V-1	580	15	..	..	6.14
		30	134	640	6.01
V-2	480	30	125	670	6.10
V-3	400	15	..	..	6.56
		30	..	..	6.11
V-4	280	30	122	..	6.22
V-5	245	30	119	..	6.26
V-6	155	30	103	710	7.19

[a] See footnote c of Table VI.

Theoretical expositions on the elastic properties of polymeric networks such as exist in vulcanized rubbers in general have dealt only superficially with the influence of the quantitative aspects of the network structure. The "equation



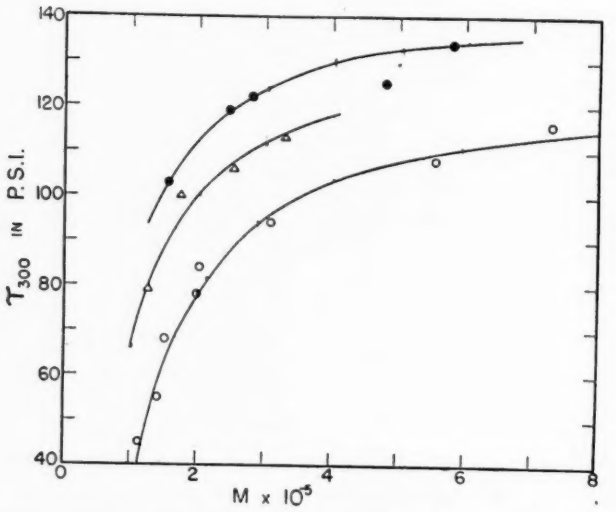


FIG. 6 (*Above*).—Tension at 300 per cent elongation ("modulus" at 300 per cent) *vs.* molecular weight M (or $\overline{M}_n$) before vulcanization.

FIG. 7 (*Below*).—Tension ("modulus") at 300 per cent elongation *vs.* reciprocal of molecular weight M (or $\overline{M}_n$).

○ Low unsaturation fractions
◑ Unfractionated polymer II–A
△ High-unsaturation fractions from polymer IV
● High-unsaturation fractions from polymer V

of state" for vulcanized rubber has been expressed[23] in the form:

$$\tau = (RT\nu/V)(\alpha - 1/\alpha^2) \tag{13}$$

That is:

$$G = RT\nu/V \tag{14}$$

where R is the gas constant, T is the absolute temperature, and ν is the number of "molecules" or, more accurately, the effective number of chain elements in volume V of the network. The effect of the finite molecular weight of the primary molecules is neglected in these formulas, although in one instance[16] the assumption that the primary molecules are infinitely long was mentioned specifically. When this is the case, ν will equal the number, ν_0, of cross-linked units or half the number of cross-linkages. Equations 13 and 14 have led to the expectation, therefore, that the "modulus" (and G) should be proportional to the degree of cross-linking (inversely proportional to M_c), and no particular importance has been attached to the molecular weight M of the primary molecules.

The experimental modulus values in Tables VI and VII and plotted against M in Figure 6 show that molecular weight M is a more critical factor than the degree of cross-linking over the range covered by these results. The quantitative effects of these factors will be examined in greater detail in the following sections.

Effect of Molecular Weight on Modulus.—If the cross-linking index γ, representing the number of cross-linked units per primary molecule in the vulcanizate, is not very large, the occurrence of terminal chains and related network imperfections or flaws materially reduces the number of effective chains below ν_0, the number which would be present if M were infinite. This effect of finite molecular weight can be taken into account[17] by considering that some of the cross-linkages are, in effect, required to combine the N primary molecules into a single ramified molecule devoid of circuitous connections. The number required for this purpose is equal to N. Cross-linkages in addition to this number provide internal connections between different parts of the structure, and in this way produce a structure which can be correctly designated as a network. Only cross-linkages in excess of the number of primary molecules effectively "fix" the structure so it responds elastically to deformation. The effective number of cross-linkages is given therefore by $\nu_0/2 - N$. The effective number of chains, ν, is equal to twice the effective number of cross-linkages or number of circuitous connections in the network. (A similar, more detailed treatment of the effects of network imperfections has already been published[17]). Hence:

$$\nu = \nu_0 - 2N = \nu_0 - 2\rho V/M \tag{15}$$

where ρV is the weight of polymer containing N primary molecules. Introducing Equation 15 into 13, the retractive force per unit initial cross-sectional area becomes:

$$\begin{aligned} \tau &= (RT/V)(\nu_0 - 2\rho V/M)\varphi(\alpha) \\ &= (RT\rho/M_c)(1 - 2M_c/M)\varphi(\alpha) \end{aligned} \tag{16}$$

$$G = (RT\rho/M_c)(1 - 2M_c/M) \tag{17}$$

The above derivation of the simple factor $(1 - 2M_c/M)$ to express the dependence of modulus on M is well founded as long as M is sufficiently greater than M_c to render the residual sol fraction small. This requires that M be at

least three times M_c[15]. Otherwise the disproportionate distribution of cross-linkages between sol and gel[24] must be taken into account.

In the above analysis of the effect of finite molecular weight on elastic properties, it is the number of primary molecules which enters the equations. Hence, if the polymer is heterogeneous with respect to molecular weight, M is to be replaced by the number average $\overline{M}_n$.

According to Equations 16 and 17, fractions of the same unsaturation but differing in molecular weight should produce vulcanizates the moduli of which vary linearly with the reciprocal of M. In Figure 7 the 300 per cent "modulus" figures of Tables VI and VII are plotted against $1/M$. Results for fractions from polymers I, II, and III are sufficiently concordant, in spite of the minor differences in their unsaturations indicated by the determinations summarized in Table I, to permit them to be considered together without differentiation. They substantiate the predicted linear relationship. The modulus of the unfractionated polymer II–A agrees well with the results for fractions when compared according to its number average.

Results for high-unsaturation fractions from polymers IV and V do not coincide, presumably owing to the difference in their unsaturations (Table I). Separate straight lines are drawn in Figure 7 through these two sets of points. Owing to the limited number of points and the irregularities which occur (probably due principally to poor reproducibility in the curing operation), the straight lines drawn for these polymers are to be considered merely as rough approximations.

The equations of the three straight lines drawn in Figure 7 can be expressed as follows. For the low-unsaturation fractions:

$$\tau_{300} \text{ per cent} = 127(1 - 74{,}000/M) \tag{16A}$$

For the high-unsaturation fractions, polymer IV:

$$\tau_{300} \text{ per cent} = 135(1 - 52{,}000/M) \tag{16B}$$

and for polymer V:

$$\tau_{300} \text{ per cent} = 145(1 - 45{,}000/M) \tag{16C}$$

All are expressed in pounds per square inch. Comparing these with theoretical Equation 16 or 17, M_c values for the respective polymers are 37,000, 26,000, and 22,500. The agreement with the previous independent estimates, 35,000 and 20,000, respectively, for the low (I, II, and III) and high (IV) unsaturation polymers, is good. The differences are within the experimental errors attending either method for determining M_c. Thus the above theoretical explanation for the contribution of initial molecular weight to elastic properties is confirmed and the previous estimates for the M_c's are substantiated.

Effect of Degree of Cross-Linking on Modulus.—On further examination of empirical Equations 16A, 16B, and 16C it is found that the intercepts for $M = \infty$ (corresponding to the initial numerical factors in these equations) do not agree with theoretical Equation 16, according to which they should equal $(RT\rho/M_c)\varphi(\alpha)$. Setting $\alpha = 4$ in $\varphi(\alpha)$, as given by Equation 12, and substituting the M_c values from the above paragraph, these factors are calculated to be 35, 50, and 58 pounds per square inch, compared with the observed 127, 135, and 145, respectively. The differences in magnitude might be excused, in part at least, on the grounds that the statistical mechanical procedure employed in deriving Equation 13, from which Equation 16 was obtained by introducing the above correction for finite molecular weight, is fundamentally only

approximate. However, the relatively small change in "modulus" with degree of cross-linking cannot be dismissed in this way. The theory predicts explicitly that the modulus for $M = \infty$ should increase proportionally to the abundance of cross-linkages (inversely proportional to M_c). High-unsaturation polymer V contains at least 50 per cent more cross-linkages than the low unsaturation polymers, yet its modulus extrapolated to infinite molecular weight is only 14 per cent greater.

It has been suggested[17] that these discrepancies are caused by entanglements of chains in the network structure. Two or more chains, though not bonded together at any point, may be looped about one another in such a way that they cannot be disentangled without rupture of a primary valence bond. These entanglements restrict the number of configurations which the chains are able to assume, and the elastic response of the network to deformation are augmented by them; they should act in effect like additional cross-linkages. In the absence of primary valence cross-linkages, however, permanent entanglements could not exist[17]. (It can be shown readily that these entanglements would not alter the correction factor introduced previously for finite molecular weight; terminal chains cannot become involved in permanent entanglements[17].

It would be expected further that the relative contribution of entanglements to the retractive force should be greater, the longer the chains. The increase in modulus with degree of cross-linking (decrease in M_c) predicted by Equations 16 and 17 should be partly compensated by a decrease in the entanglement factor, therefore. In other words, the discrepancies between observed and calculated "moduli" should decrease as the degree of cross-linking is increased; this is observed to be the case.

Stress-Strain Curves at High Elongations.—At elongations of 400 to 700 per cent the stress-strain curves (Figure 5) assume pronounced upward curvature until a steep upward slope has been reached. Thereafter the curves proceed almost linearly to their breaking points; only the onset of these final portions of the curves are included in Figure 5.

Another noteworthy feature of the stress-strain curves in the region of steep ascent is their parallelism to one another; their final slopes above about 500 pounds per square inch are roughly of the same magnitude, independent of initial molecular weight and degree of cross-linking. The location along the elongation axis of the steep, linear portion of the stress-strain curve is, of course, displaced for one polymer as compared to another, depending on the vulcanizate structure. As an index of the location of the region where the stress-strain curve assumes steep upward curvature, the elongations at which the tension reaches 500 pounds per square inch are recorded in Tables VI and VII. For samples of about the same tensile strength these figures are directly related to their ultimate elongations, since stress-strain curves for all pure-gum Butyl vulcanizates are approximately parallel and linear from this tension to the breaking point.

The elongations at 500 pounds per square inch do not correlate directly with the 300 per cent modulus over variations in initial molecular weight and in degree of cross-linking. For example, a low-unsaturation and a high-unsaturation vulcanizate (the latter from a fraction of much lower molecular weight) which show identical stress-strain curves up to 400 per cent elongation, as indicated by their moduli at 300 per cent in the tables, do not reach 500 pounds per square inch at the same elongation. A lower elongation is required for the latter. Observations such as these are further indications of the fact that the stress-strain curves in general are not rendered superimposable throughout all

elongations by adjusting their stress scales by suitable factors. It is apparent that the "modulus" up to 400 per cent elongation and the position of the steep rise in the stress-strain curve depend in different manner on the structure of the vulcanizate.

Butyl, like natural rubber, becomes crystalline on stretching. As would be expected, it shows the same crystal pattern[11] with x-rays found for polyisobutylene and analyzed by Fuller and co-workers[25]. In pure-gum vulcanizates of good-quality unfractionated Butyl the first vestiges of a crystal pattern become apparent in the x-ray diagram at elongations in the neighborhood of 500 per cent. A smaller degree of crystallinity, not detected by x-ray diffraction, may occur at somewhat lower elongations.

Field[16] showed that the x-ray diagram acquires the characteristic oriented fiber pattern coincident with the increase in slope in the stress-strain curve of natural rubber gum vulcanizates. The degree of crystallinity which he computed from the x-ray patterns increases rapidly in this region. The percentage of crystalline polymer approaches an asymptotic value (around 80 per cent) which changes little with further elongation over the subsequent fairly linear portion of the stress-strain curve extending to the breaking point. Results of Dart and Guth[26] on thermoelastic effects in the fast stretching of Butyl supply further evidence for the rapid acquisition of crystallinity at high elongations. Unfortunately their results did not include suitable stress-strain curves for comparison.

The pronounced upward curvature in the stress-strain curves for Butyl in the region of 400 to 700 per cent elongation, depending on the sample, is doubtless due to the occurrence of crystallization. The final steep ascent of the curve just beyond this region and extending to the breaking point indicates a high degree of crystallinity. In the light of Field's results on natural rubber, we consider that over this almost linear portion of the curve the degree of crystallinity remains almost constant at a value near its asymptotic limit. The similarity in the slopes of the curves in this region suggests roughly similar degrees of crystallinity in different samples. (It is not meant to suggest, however, that they are quantitatively the same regardless of structure.) The elongations at 500 pounds per square inch are considered to represent the points at which about the same (high) degree of crystallinity is developed in different Butyl vulcanizates.

Crystallization would be expected to depend on the average degree of orientation produced by elongation. For chains which exist in more or less random configurations when the network is not deformed, it can be shown that the average degree of alignment produced by a given elongation is greater, the lower the average length of the chain, M_c. Hence, it is to be expected that, with greater degrees of cross-linking, crystallization sets in at lower elongations. The results agree with this deduction. Even when comparison is made between low- and high-unsaturation polymers having molecular weights such that the numbers (γ) of cross-linked units per primary molecule are about the same, the latter are found to undergo crystallization, as indicated by the point at which the tension reaches 500 pounds per square inch, at lower elongations (Tables VI and VII).

The increase in the elongation for incipient crystallization with decrease in molecular weight is believed to arise mainly from the concurrent increase in the proportion of terminal chains (Equation 9). These are not subject to permanent orientation when the rubber is stretched; hence, they are not likely to enter into crystallite formation. They can be expected to act like amorphous

diluents which not only are themselves reluctant to enter into crystallite formation, but which also repress crystallization of the remainder of the structure. In addition, the average lengths of the elastically effective chain elements of the structure is increased somewhat, owing to other types of network "flaws"[17], as M decreases. This factor also tends to decrease the average orientation at a given elongation, for the reason given in the preceding paragraph.

EQUILIBRIUM SWELLING OF VULCANIZATES

Relationship of Swelling Capacity to Vulcanizate Structure.—When vulcanized rubber is placed in a liquid of similar chemical composition, the former absorbs the latter until a state of equilibrium is reached between swollen rubber and supernatant excess liquid. At this point the gain in entropy afforded by further dilution of the rubber is exactly balanced by the decrease in entropy which would attend further expansion of the network. Swelling of the network is analogous to deformation, with the difference merely that during swelling the network is extended istropically in three dimensions. The reaction of the network to swelling, like that to deformation, originates in the decrease in the statistical probability of extended configurations of the network chains.

According to a theoretical treatment of swelling of cross-linked networks recently developed[27] along the same lines as the elasticity theory referred to above, the equilibrium "swelling ratio" (SR), representing the volume of swollen polymer at equilibrium divided by the volume of the dry polymer contained therein, bears a direct relationship to the (effective) number ν of chains. With suitable mathematical simplifications appropriate when the swelling ratio is large, this relationship reduces to the convenient (though slightly approximate) form:

$$SR = [(1-2\mu)V/2\nu V_1]^{3/5} \tag{18}$$

where μ is a semiempirical parameter[28] characteristic of a given solvent-solute pair, and V_1 is the molar volume of the solvent. Substituting from Equation 15 for the "corrected" number of chains, ν, exactly as was done in deducing Equation 16:

$$(1/SR)^{5/3} = \left[\frac{2\rho V_1}{(1-2\mu)M_c}\right](1 - 2M_c/M) \tag{19}$$

The similarities of this equation to Equation 16 are apparent; taking $(1/SR)^{5/3}$ as the analog of the retractive force of Equation 16, both quantities depend inversely on M_c and directly on the same correction factor for finite molecular weight.

Swelling ratios in cyclohexane at 25° C for various vulcanized Butyl fractions and mixtures of fractions are included in Tables VI and VII. In Figure 8 $(1/SR)^{5/3}$ is plotted against $1/M$, or $1/\overline{M}_n$ for the heterogeneous polymers. The points for the low-unsaturation polymers describe a straight line, in accordance with Equation 19. The mixtures of fractions, and unfractionated polymer II-A as well, fall on the same line when their number averages are employed, showing that swelling, like modulus, also depends on this average explicitly. The points for high-unsaturation polymers IV and V again are sufficient only for locating approximate lines through them. The equations

of the lines drawn in Figure 8 follow: For the low-unsaturation polymers:

$$(1/SR)^{5/3} = 0.0506(1 - 78{,}000/M) \quad (19A)$$

For polymer IV,

$$(1/SR)^{5/3} = 0.0540(1 - 52{,}000/M) \quad (19B)$$

For polymer V,

$$(1/SR)^{5/3} = 0.0556(1 - 47{,}000/M) \quad (19C)$$

The values of M_c indicated by these equations (39,000, 26,000, and 23,500, respectively) are in good agreement with those previously deduced. The first coefficients of these equations, like those of 16A, B, C, do not agree with theory in that they do not vary in proportion to $1/M_c$. The previous explanation advanced for the similar anomaly in the "modulus" values should be equally applicable here.

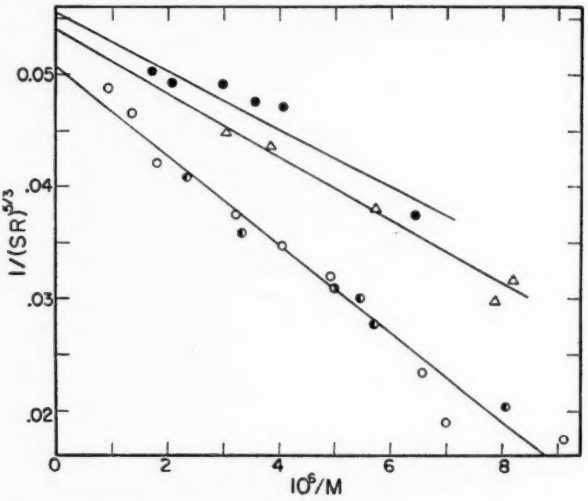


FIG. 8.—Reciprocal of the 5/3 power of swelling ratio *vs.* reciprocal of M or $\overline{M}_n$.
○ Low unsaturation fractions
◐ Mixtures of low-unsaturation fraction
◑ Unfractionated polymer II–A
△ High-unsaturation fractions from polymer IV
● High-unsaturation fractions from polymer V

Relationship between Modulus and Swelling.—Since the "modulus" and the swelling ratio are similarly related to the structure variables M_c and M, they can be related directly to one another. Combining Equations 16 and 19 for this purpose:

$$\tau_\alpha = RT(1 - 2\mu)\varphi(\alpha)/[2V_1(SR)^{5/3}] \quad (20)$$

i.e., the tension at a given elongation is predicted to be inversely proportional to the 5/3 power of the swelling ratio. The existence of some sort of inverse relationship between modulus and swelling capacity has been recognized for some time. Scott[29], for example, pointed out that, for a series of cures of natural rubber, the maximum in modulus and the minimum in swelling coincide.

To demonstrate the quantitative significance of Equation 20, the "modulus" at 300 per cent elongation is plotted in Figure 9 against the log of the swelling

ratio for various Butyl pure-gum vulcanizates. The straight line has been drawn with the theoretical slope $-5/3$. The experimental points, which include Butyls differing in unsaturation, molecular weight, and molecular weight heterogeneity, agree satisfactorily with this theoretically predicted relationship.

The irregular deviations which occur are somewhat smaller in general than those in Figures 7 and 8, representing, respectively, the modulus-molecular weight and the swelling ratio-molecular weight relationships. The greatest single source of error in this work is believed to have originated from a certain lack of reproducibility in the curing process. When the one physical property is compared with the other as in Figure 9, errors of this type do not appear—hence, the opportunity for the greater uniformity of results exhibited here.

The experimental confirmation of Equation 20 furnishes proof that the structural factors responsible for the elastic retractive force are quantitatively

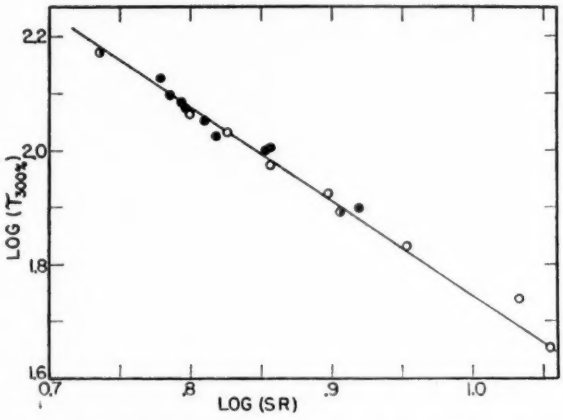


FIG. 9.—Log-log plot of modulus at 300 per cent elongation *vs.* swelling ratio.
○ Low-unsaturation fractions
◑ Unfractionated polymers
● High unsaturation fractions

the same as those which operate in controlling the degree of swelling. Exactly the same cross-linkages and entanglements which are operative in elastic deformation are also effective in limiting the equilibrium degree of swelling in the presence of solvent. Hence, their existence cannot depend on van der Waals interactions, which would certainly be overcome by the swelling agent.

By comparing the equation of the line in Figure 9:

$$\log \tau_{300} = 3.41 - 1.67 \log (SR)$$

with theoretical Equation 20, μ is found to be 0.30. This is less than the value 0.42[30] obtained from osmotic pressure measurements on dilute solutions of polyisobutylene in cyclohexane[31].

TENSILE STRENGTHS

Fractions of Low Unsaturation.—Table VIII gives tensile strengths for pure-gum cured fraction from Butyl polymers I, II, and III. The molecular weights in the second column have been computed from the intrinsic viscosities after compounding (Table II). Vulcanizates prepared from fractions below a

TABLE VIII

TENSILE STRENGTHS OF LOW-UNSATURATION BUTYL FRACTIONS
(CURED AT 307° F)

Polymer fraction	$M \times 10^{-3}$ (after compounding)	Cured 30 min.[a] Tensile strength, (lb. per sq. in.)	Cured 30 min.[a] Elongation (%)	Cured 60 min.[a] Tensile strength, (lb. per sq. in.)	Cured 60 min.[a] Elongation (%)
Pure-Gum Cures					
I-1	1080	4750	950	4400	975
I-2	730	4100	950	4350	975
I-3	690	..	..	4200	1050
I-4	650	4300	1075	4100	1025
I-5	555	4325	1000	4425	975
II-2	390	..	..	4300	1025
II-3	310	3625	1050	3875	1000
II-4	285	3580	1075	3580	1025
II-5	245	2950	1090	..	..
III-1	245	2560	1075	2950	1090
III-3	210	..	..	3150	1000
II-7	202	2850	1050	3200	1050
III-4	185	2200	1150	2850	1100
II-9	152	650	1100	1450	1050
II-10	152	..	..	1700	1050
III-6	143	1650	1100	1700	1025
II-13	108	..	..	89	825
III-8	108	52	770	130	825
III-10	85	..	..	110	950
III-11	81	..	..	50	775
Fractions compounded with 50 parts of black[b]					
I-4	715[b]	3400	800	3420	775
II-2	410	3340	800	3450	785
II-6	285	2850	900	2900	850
III-2	265	..	..	3000	825
II-8	172	2390	800	2840	800
III-5	168	2300	..	2650	850
III-7	116	850	800	1960	900
III-9	94	..	..	940	700
III-12	57	..	..	145	500
III-15	42.5	..	..	67	400
III-18	25.8	..	..	Uncured (sol.)	

[a] Tensile strengths and ultimate elongations represent mean values obtained with two or more dumbbells from the same cure.

[b] Intrinsic viscosities could not be run on the compounded sample due to partial insolubility resulting from carbon black.

molecular weight of 75,000 were too fragile to be removed from the molds. At a molecular weight of 100,000 the tensile strength (60-minute cure) is roughly 100 pounds per square inch. Tensile strength increases rapidly with increase in molecular weight immediately above 100,000, reaching 1500 pounds per square inch at about 150,000, and 3000 pounds per square inch at about 200,000 molecular weight. Proceeding to higher molecular weights, the tensile strengths increase more gradually, approaching what appears to be an asymptotic value well above 4000 pounds per square inch at molecular weights beyond 400,000. Figure 10 shows these results.

There is little difference between the 30- and 60-minute cures. In the low-molecular-weight range, tensile strengths of the former fall below those for the longer cure, but at high molecular weights the tensile strengths for the 30- and 60-minute cures are indistinguishable.

Corresponding results for some of the low-unsaturation fractions compounded with 50 parts of carbon black according to the recipe given earlier in the paper are presented in the lower portion of Table VIII and in Figure 11. Above about 30,000 molecular weight the rubber was rendered partially insoluble by vulcanization. Tensile strength is developed at lower molecular

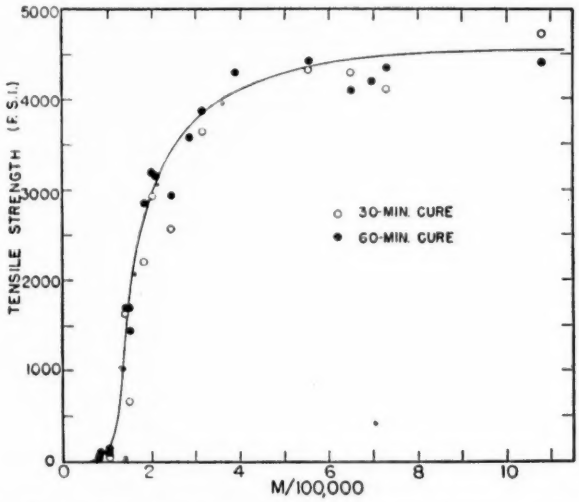


Fig. 5

FIG. 10.—Tensile strength of pure-gum vulcanizates of low-unsaturation fractions *vs.* molecular weight.

weights than for the pure-gum vulcanizates, 100 pounds per square inch being reached at a molecular weight of about 50,000 on the 60-minute cure. A tensile strength of 300 pounds is again approached at a molecular weight of about 200,000, but at higher molecular weights the tensile strengths are considerably lower than those obtained with the pure-gum recipe.

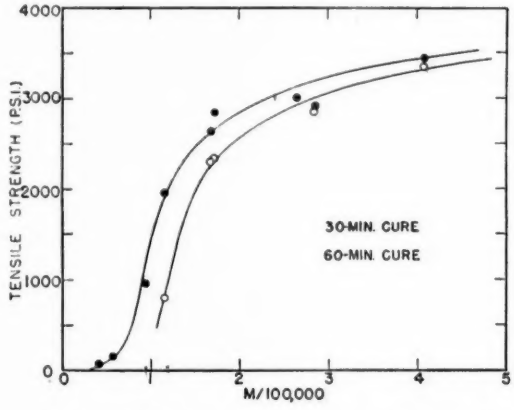


Fig. 6

FIG. 11.—Tensile strength of low-unsaturation vulcanizates containing 50 parts carbon black *vs.* molecular weight.

Fractions of High Unsaturation.—Table IX and Figure 12 give tensile strengths and ultimate elongations for cured fractions from polymers IV and V. The onset of measurable tensile strength occurs at a lower molecular weight than for the low-unsaturation Butyls; tensile strengths of 100 pounds per square

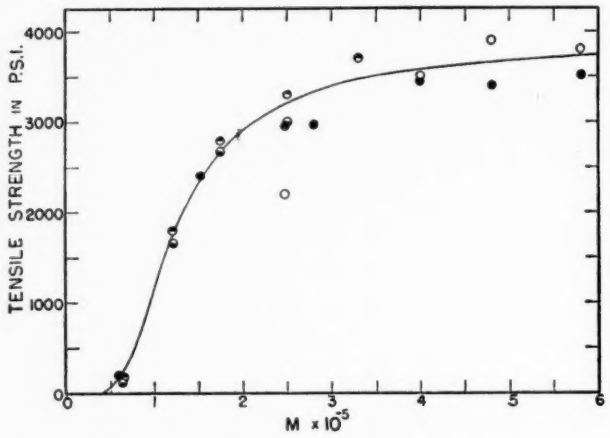


Fig. 12.—Tensile strength of pure-gum vulcanizates of high-unsaturation fractions *vs.* molecular weight.
◒ Polymer IV, 20-min. cures
◓ Polymer IV, 40-min. cures
○ Polymer V, 15-min. cures
● Polymer V, 30-min. cures

TABLE IX

TENSILE STRENGTHS OF HIGH-UNSATURATION FRACTIONS
(PURE-GUM CURES)

Polymer fraction	$M \times 10^{-3}$ (after compounding)	Time of cure (min. at 307° F)	Tensile strength[a], (lb. per sq. in.)	Elongation[a], (%)
V-1	580	15	3800	925
		30	3500	850
V-2	480	15	3900	925
		30	3400	850
V-3	400	15	3500	960
		30	3450	850
IV-1	330	40	3700	900
V-4	280	30	2970	900
IV-2	250	20	3000	1000
		40	3300	925
V-5	245	15	2200	925
		30	2950	890
IV-3	175	20	2680	990
		40	2800	1000
V-6	155	30	2400	925
IV-5	122	20	1680	1040
		40	1800	925
IV-6	64	20	115	800
		40	150	750
V-7	60	30	200	700
V-8	48.5	30	Very weak vulcanizate[b]	
IV-7	46.5	40	Very weak vulcanizate[b]	

[a] The tensile strength and ultimate elongation figures represent mean values obtained with two or more dumbbells from the same cure.
[b] Vulcanizates too fragile to be removed undamaged from the mold.

inch are acquired in the vicinity of 60,000 molecular weight, as compared with 100,000 for the low-unsaturation polymers. The tensile strength curve then rises somewhat less abruptly with increasing molecular weight.

The ultimate tensile strengths attained at high molecular weights are definitely lower than for the low-unsaturation polymers. Results for polymer V fractions point to slightly higher strengths at lower cures in the region of high molecular weights. The deficiency of the tensile strengths of these polymers compared with the low-unsaturation series cannot, however, be entirely overcome by undercuring. Other experiments not reported here, in which polymers of higher unsaturation than polymer V were included, demonstrate that at the same (high) molecular weight an increase in diolefin content beyond 1.0 per cent decreases the tensile strength, regardless of degree of cure.

TABLE X

TENSILE STRENGTHS OF MIXTURES OF LOW-UNSATURATION BUTYL FRACTIONS (PURE-GUM CURES, 60 MINUTES AT 307° F)

Designation[a]	Percentage of polymer of lower mol. wt.	$\bar{M}_n \times 10^{-3}$ calcd.[b]	Tensile strength[c], (lb. per sq. in.)	Elongation[c], (%)
I-3	0	805	4200	1050
A-1	10	325	4150	1025
A-2	20	300	3200	1025
A-3	40	183	2800	1075
A-4	65	124	1650	1100
III-10	100	85	110	950
II-2	0	410	4300	1025
B-1	25	280	3540	1025
B-2	50	210	3200	1060
B-3	75	171	2750	1060
II-10	100	143	1700	1050
II-1	0	625	..	..
C-1	10	210	3650	1000
C-2	20	126	2800	1075
C-3	35	79	1830	1100
III-17	100	30	0	..
I-6	0	580	4000	1025
D-1	40	240	3200	1050
D-2	65	175	2600	1100
II-11	100	127	..	..

[a] See Tables II and IV.
[b] Number averages calculated from molecular weights of the individual fractions before compounding. See the discussion of this point in the Experimental part of the paper.
[c] Tensile strengths and ultimate elongations represent mean values obtained with two or more dumbbells of the same cure.

Heterogeneous Mixtures of Fractions.—Table X lists tensile strengths and ultimate elongations for mixtures of low-unsaturation fractions, prepared as discussed in connection with Table IV. In Figure 13 the curve previously drawn in Figure 10 to represent the tensile strength-molecular weight relationship for individual fractions is duplicated for comparison with the results for mixtures. When the tensile strengths of the mixtures are plotted against their number-average molecular weights, given in Table X (from Table IV), the points in general follow the course of the curve for individual fractions. Only the samples of series C deviate seriously from the curve. In all other

instances the departures from the curve are no greater than the prevailing experimental irregularities. Plots of the tensile strengths of the mixtures against their weight- or viscosity-average molecular weights (Table IV) lead to much larger deviations, all points being shifted well to the right of the curve in Figure 13.

The failure of the results for series C to agree with the tensile strengths deduced in the above manner from their number-average molecular weights is due to the low molecular weight of the lower-component fraction from which these mixtures were prepared. Its molecular weight, 30,000, is less than M_c, which according to the previous estimates is about 37,000 in low-unsaturation vulcanizates. A considerable proportion of these molecules consequently survive the vulcanization process without acquiring any cross-linkages. These molecules exist as diluents dispersed in the network structure. It cannot be expected that their influence on physical properties would be equivalent to that of components which "co-vulcanize" with the network structure.

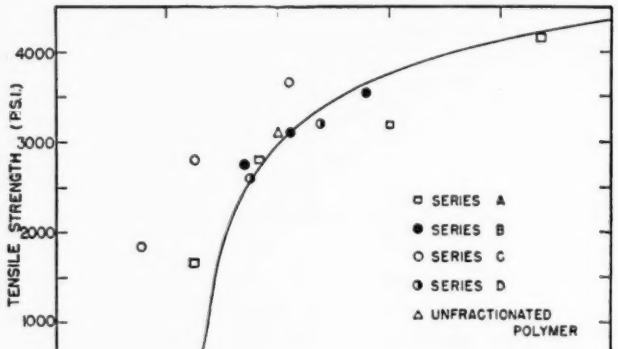


FIG. 13.—Tensile strengths obtained from mixtures of low-unsaturation fractions (Table X)

The curve is a duplicate of the one for homogeneous fractions in Figure 10.

Confirming the predicted partial nonreaction of the low-molecular-weight component in these mixtures, the soluble material extractable (with cyclohexane) from vulcanizates C-2 and C-3 was exceptionally high—9.5 and 16.1 per cent, respectively. These figures correspond to 47.5 and 46 per cent, respectively, of the total amounts of the low-polymer components in the vulcanizates. Taking M_c as 37,000, the average number, γ, of cross-linked units per primary molecule of the lower component becomes 0.81. The fraction of these molecules devoid of cross-linked units is, therefore, by exp (-0.81), or 0.45. Practically all of the cross-linked molecules are bound to the network, as a consequence of the preponderance of the component of higher molecular weight. Hence, the percentage of the lower component which remains soluble should be about 45. The observed percentages are in good agreement with this figure.

When compounded and vulcanized, unfractionated polymer II-A yielded a tensile strength of 3100 pounds per square inch. When this value is plotted

in Figure 13 against its number-average molecular weight (200,000), good agreement with the curve established for the fractions is secured. This result therefore confirms the conclusion to be derived from the results on mixtures of fractions—namely, that tensile strength is an explicit function of the number-average molecular weight being otherwise independent of the particular molecular weight distribution. Qualification is necessary, however, when the heterogeneous polymer contains an appreciable fraction of molecules too low in molecular weight to be united with the network structure.

Effect of Nonvulcanizable Ingredients.—The effects of nonnetwork components on tensile strength is made clearer by results obtained on mixtures of Butyl with ingredients which are incapable of entering into the vulcanization reaction. Two polyisobutylene fractions, one of intermediate and the other of low molecular weight, and a refined petroleum distillate, Primol-D, were compounded with separate portions of Butyl fraction I-3. Table XI lists the compositions of these mixtures, their tensile strengths, and ultimate elongations. The nonvulcanizable ingredients were almost quantitatively extractable.

The outstanding result in Table XI is the independence of the tensile

TABLE XI

TENSILE STRENGTHS OF MIXTURES OF BUTYL FRACTION I-3 WITH POLYISOBUTYLENES AND PRIMOL-D (CURED 60 MINUTES AT 307° F)

Added component				[η] of mixt. (calcd.)	[η] observed after compounding	Per cent sol[a] after vulcanization	Tensile strength (lg. per sq. in.)	Elongation (%)
Designation	[η]	$M \times 10^{-3}$	Per cent of mixt.					
None added	..	..	..	2.18	1.98	..	4200	1050
Polyisobutylene (8–10)	0.75	150	15	1.96	1.79	15	3250	1050
			30	1.75	1.56	27	2250	1075
Polyisobutylene (18–25)	0.30	37	15	1.90	1.69	11	3100	1100
			30	1.62	1.47	25	2200	1100
Primol-D	..	..	15	1.85	..	..	3200	1100
	..	..	30	1.53	..	32	2100	1150

[a] Extracted 8 days with cyclohexane at room temperature.

strength on the molecular weight of the added nonreactive ingredient; regardless of whether polyisobutylene of 150,000 molecular weight or Primol-D with a molecular weight of only a few hundred is employed, the same tensile strength, within experimental error, is observed for the same weight percentage of nonvulcanizable ingredient. In view of this result it is obviously impossible to include nonnetwork ingredients in the number-averaging rule given earlier.

DISCUSSION OF TENSILE STRENGTH RESULTS

No adequate theory of tensile strength in high polymers exists at present. Proceeding from a phenomenological point of view, it is noteworthy that in Butyl, as in natural rubber, relatively little tension is developed until high elongations are reached, whereupon there is an enormous increase in stiffness, the tension rising rapidly with further elongation. The rubber acquires to a considerable degree the characteristics of a textile fiber. (The tensile strengths of the best fibers of silk and cellulose are in the range 50,000 to 100,000 pounds per square inch. Butyl fractions of high molecular weight register tensile strengths of over 40,000 pounds based on the cross-section at break.) Obviously, it is this region of the stress-strain curve which is of primary importance with respect to strength.

The connection between crystallization and the transformation of the rubber from a soft, easily deformed material into a hard, fibrous substance was pointed out earlier in the paper; throughout the steep portion of the stress-strain curve the rubber is considered to be highly crystalline. As pointed out frequently in the literature on natural rubber, this circumstance suggests an intimate connection between crystallization and high strength. In support of this view, the tensile strength of either Butyl or natural rubber is very small at temperatures such that crystallization does not occur on stretching (pure-gum cures). Furthermore, synthetic rubbers which do not crystallize when stretched generally exhibit low strengths, except when compounded with a reinforcing pigment such as carbon black. Their stress-strain curves possess no final steep portion. Partial exceptions are found in certain elastomers having relatively high brittle points (alternatively, when the temperature of measurement is not far above the brittle temperature); they exhibit intermediate strengths, at the sacrifice, however, of high elongation. Their superiority in strength compared with other noncrystallizing rubbers may be the result of embrittlement induced by stretching.

On considering the effects of deformation on the structure of the noncrystalline and "fluid" (as opposed to brittle) rubber, it is clear that the chains easily slip from one configuration to another in whatever manner best alleviates the imposed stresses. Owing to the irregularity of the loose network structure, elongation inevitably induces widely varying degrees of orientation in various elements of the structure, with corresponding inequalities in the distribution of stresses among chains. Only a minute fraction of the chemical bonds in any particular section of the rubber need be broken to destroy the continuity of the network structure. Thus, in a given portion of the network structure, where the stresses borne by the chains happen to be excessively above average, breakage of only a few chemical bonds eliminates reaction (of this part of the network) to the applied stress. Thus, in effect, a relatively few bonds withstand the stress.

When elongation induces crystallization, oriented chains are bound together in crystallites. The aggregate lateral van der Waals forces between adjacent chains in the crystallites virtually eliminate longitudinal slippage of a chain relative to its neighbors within the crystallite[32], although there is relatively little resistance to lateral separation of the chains. Thus, crystallization improves orientation of portions of the chains entering the crystallites, and at the same time it impedes longitudinal slippage of the chains. An appreciable fraction of amorphous material remains, and conceivably rupture may eventually originate in these regions. However, many valence bonds must be broken to accomplish the onset of complete failure of the sample. The amorphous regions contain numerous "chains" leading from one crystallite to another, each crystallite functioning as a giant cross-linkage which binds together ends of these chains. In other words, the stresses in the amorphous regions are borne by many chains, and failure of the sample cannot occur through rupture of a few of them. An extension of these arguments to a rubber which embrittles on stretching is obvious.

In view of the dominant importance of crystallization in relation to strength, it seemed appropriate in the course of the analysis of the results given above to explore the postulate that tensile strength should be dependent on the proportion of the vulcanizate which is oriented by stretching and, therefore, susceptible to crystallization. According to Equation 9 the fraction of the vulcanizate occurring in principal network chains, exclusive of terminal chains which

are not permanently oriented by stretching, is given by:

$$w_A = 1 - 2M_e/(M + M_e) \tag{21}$$

If the molecules are heterogeneous in length, M is to be replaced by the number average $\overline{M}_n$ since it is the number of primary molecules which is of concern, as shown in the course of the derivation of Equation 9. The tensile strength could be expected, therefore, to depend explicitly on the number-average molecular weight, in accordance with observation.

If it is postulated further that the tensile strength should increase linearly with the fraction w_A of "active" network, then according to Equation 9 or 21 the tensile strength should decrease linearly with $1/(M + M_e)$, which is about equivalent to $1/M$ except when M is small. In Figure 14 the tensile strengths

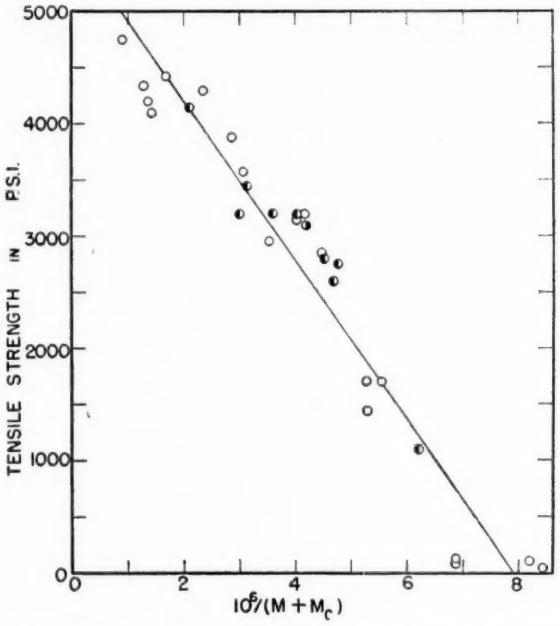


FIG. 14.—Tensile strength of low-unsaturation fractions and mixtures after pure-gum cure *vs.* $1/(M + M_e)$, or $1/(\overline{M}_n + M_e)$.
○ Fractions
◐ Mixtures of fractions
◑ Unfractionated polymer II-A

for the low-unsaturation fractions and their mixtures are plotted against $1/(M + M_e)$, M_e being taken equal to 37,000. The points are in surprisingly good accord with the postulated linear relationship. There is some indication of curvature, but this may not be beyond the experimental error. The equation of the straight line drawn in Figure 14 can be expressed:

$$\text{Tensile strength in pounds per square inch} = 5600[1 - 126{,}000/(M + 37{,}000)] \tag{22}$$

A plot against $1/M$ is about equally satisfactory; *i.e.*, within the limits of ex-

perimental errors the tensile strength varies linearly with the reciprocal of M or $\overline{M}_n$ at constant degree of cross-linking.

The linear relationship between the fraction w_A of the material which is oriented by stretching is not a direct proportionality. If this were the case, the tensile strength would reach zero at $M = M_c$; the observed linear relationship extrapolates to zero at $M = 89{,}000$ (Equation 22). At this molecular weight, according to Equation 21 with $M_c = 37{,}000$, $w_A = 0.41$; *i.e.*, about 41 per cent of the vulcanized polymer is subject to permanent orientation when stretched. If Equation 21 is incorporated into 22, again with $M_c = 37{,}000$, the tensile strength relationship can be expressed in terms of the fraction of orientable materials as follows:

$$\text{Tensile strength} = 9540(w_A - 0.413) \qquad (22A)$$

It is understandable that tensile strength should virtually vanish with decrease in molecular weight well in advance of the disappearance of the orientable fraction of the structure. The unoriented portion of the structure depresses the tendency of the oriented portion to crystallize on stretching. If the former somewhat exceeds the latter, rupture occurs before the material can be induced to crystallize by stretching. In Figure 5, for example, the stress-strain curve for the vulcanizate of 110,000 molecular weight shows no evidence of crystallization (as pointed out in the previous discussion of stress-strain curves at high elongations). Owing to the high proportion $(1 - w_A)$ of terminal chains, an excessive elongation presumably would be required to produce crystallization. Before such elongations are reached, however, sufficient stress is developed within the poorly constructed network to produce rupture. This occurs at an elongation of about 800 per cent. The tensile strength of the material is only of the order of 100 pounds per square inch. For the development of appreciable strength a considerable fraction of the structure must be oriented by stretching.

The present tensile strength relationship should be applied literally only to vulcanizates which exhibit some vestiges, at least, of crystallization before they fail. This follows from the nature of the postulates introduced in the above quasi-theoretical treatment. It is obvious also that it cannot possibly apply in the molecular weight region below about 100,000; at an M of 89,000 the tensile strength is predicted to reach 0, but a polymer of lower molecular weight retains some strength, although it is very low—*i.e.*, less than 100 pounds per square inch. As far as the above relationship is concerned, strengths of this order are negligible.

The numerical coefficients in Equations 22 and 22A doubtless are altered by a change in temperature. At a lower temperature, for example, it is likely that appreciable tensile strength would be retained to lower molecular weights and, hence, to values of w_A less than 0.4, owing to the increased stability of the crystalline state.

The tensile strengths of cellulose acetate samples are similarly related to their molecular weights. In addition to finding that the tensile strength is an explicit function of the number-average molecular weight, Sookne and Harris[33] state that the tensile strength of a mixture of fractions can be deduced by weight averaging over the tensile strengths of the pure fractions; *i.e.*, if $(TS)_1$ and $(TS)_2$ are the tensile strengths of the pure fractions, then the tensile strength of a mixture prepared from weight fractions w_1 and w_2 can be predicted from the equation:

$$(TS)_m = w_1(TS)_1 + w_2(TS)_2$$

It can be shown (*11B*) that these apparently contradictory statements are reconcilable only if the tensile strength is related to the molecular weight of a pure fraction in accordance with

$$TS = A + B/M \tag{23}$$

where A and B are constants. Equation 23 is equivalent to Equation 22 if $1/(M + M_c)$ is replaced by $1/M$. The tensile strengths of cellulose acetate, according to the results of Sookne and Harris[33], should therefore decrease linearly with $1/\overline{M}_n$.

This similarity between the tensile strength-molecular weight dependence for a rubber, on the one hand, and for a cellulose derivative on the other is striking; the one possesses a network structure and is capable of undergoing high elongation, whereas the other contains no primary valence network and elongates relatively little. Spurlin[34] suggested that failure in fibers under stress originates from the end of molecules, which represent points of weakness in the structure. He concluded that tensile strength should depend in some manner on the number-average molecular weight. While the results on cellulose acetate are at least partially accounted for by this explanation, it fails completely if applied to the results on Butyl. Here it is the amount of nonorientable material rather than the number of ends of molecules, or number of terminal chains, which is primarily important.

The linear dependence of tensile strength on the fraction of the structure which is permanently oriented by stretching can be extended to mixtures with nonvulcanizing ingredients (Table XI). In these vulcanizates:

$$w_A = w_1[1 - 2M_c/(M + M_c)] \tag{24}$$

where w_1 is the weight fraction of Butyl polymer in the mixture. We shall assume that M_c is 37,000, being unaffected by the diluent; actually it may be increased slightly, owing to the increase in "intramolecular" cross-linkages[17] with dilution. Taking for M the observed molecular weight 690,000 of fraction I-3 after compounding without diluent (Table II), and substituting w_1 values of 0.85 and 0.70 into Equation 24, the fractions w_A of active network in the vulcanizates of Table XI are 0.764 and 0.629, respectively. Substituting these in Equation 22A, the tensile strength for the vulcanizates containing 15 per cent of nonvulcanizable diluent is calculated to be 3350 pounds per square inch, in comparison with the observed values of 3100 to 3250. For the vulcanizates containing 30 per cent of nonvulcanizable material, the tensile strength calculated in this way is 2060, compared with the observed values in the range 2100 to 2250 pounds per square inch. The agreement is all that could be expected.

Evidently the tensile strength is depressed equally (on a weight or volume basis) by terminal chains and by ingredients which are not connected by chemical bonds to the vulcanizate network. These are indistinguishable in so far as their influence on tensile strength is concerned. It now becomes clear why the molecular weight of the nonvulcanizable ingredient exerts no effect on tensile strength.

Any diluent selected indiscriminately may not necessarily produce the same effect. If an appreciable heat change accompanies the mixing of diluent with network, partial segregation on the one hand, or association on the other, may be expected to modify the tensile strength. Specifically, a diluent which mixes endothermally with the polymer may be expected to reduce the tensile strength

somewhat less than would an equal proportion of terminal chains, or of an "athermal" diluent such as one of those selected in Table XI. An exothermic diluent may effect a greater depression in the tensile strength, owing to its tendency to associate with, or adhere to, the network chains and thereby suppress crystallization.

The molecular weights at which vulcanizates from the low- and high-unsaturation polymers begin to acquire strength are approximately in inverse proportion to the concentrations of cross-linkages which they attain. For example, at molecular weights of 100,000 and 60,000, respectively, their tensile strengths reach 100 pounds per square inch; these figures are about in the ratio of their respective M_c values. In other words, the average number γ of cross-linked units per molecule required for the onset of appreciable strength appears to be about constant.

Other experiments not reported here have shown that a polymer fraction containing about 0.15 mole-percentage of isoprene and for which $M = 600{,}000$ yielded a vulcanizate (using the above pure-gum recipe) with a tensile strength of about 3000 pounds per square inch. Another fraction containing 0.30 mole-percentage of isoprene and having the same molecular weight produced a vulcanizate with a tensile strength close to 4000 pounds. Assuming that the concentration of cross-linkages varies directly as the concentration of diolefin (as indicated by certain results cited in the discussion of the structure of Butyl vulcanizates), the M_c values for these vulcanizates, by comparison with the low-unsaturation vulcanizates, should be about 12,000 and 60,000, respectively. The values of $\gamma(= M/M_c)$ for these vulcanizates should be about 5 and 10, respectively, according to this assumption. The low-unsaturation polymers which have been investigated here in some detail acquire tensile strengths of 3000 and 4000 pounds per square inch at molecular weights of about 210,000 and 400,000, respectively. The corresponding values of γ, 6 and 11, are close to those for the above-mentioned vulcanizates having corresponding tensile strengths.

While these results may be too fragmentary to justify definite conclusions, they indicate that at the same value of γ the tensile strength is the same, independent of the degree of cross-linking over the range. In other words, the tensile strength seems to depend only on the percentage of orientable material, which is very nearly proportional to $(1 - 2/\gamma)$ (Equations 9 and 21). Hence Equation 22A can be applied to polymers varying both in molecular weight and in unsaturation, within the range 0.15 to 0.5 mole-per cent.

At higher unsaturations—*i.e.*, in the range of 1.0 mole-per cent and above—Equation 22A cannot be applied. Here the maximum tensile strengths reached at high molecular weights are lower than those for vulcanizates containing fewer diolefin units. The effect is greater in polymers containing 1.5 to 2.0 mole-per cent or more of diolefin. The depression of the tensile strength with increase in the percentage of diolefin cannot be overcome entirely by undercuring; hence it must be attributed to the diolefin units themselves rather than to an excessive concentration of cross-linkages. Presumably the failure of the isoprene units to fit into the polyisobutylene crystal lattice is responsible for this effect; *i.e.*, they decrease the degree of crystallinity which can be achieved. It is rather surprising that this effect is noticeable with as little as 1 mole-per cent of isoprene.

Little has been said concerning ultimate elongation values. For a given degree of unsaturation in the polymer, they increase with M to a maximum, which occurs at an intermediate tensile strength, then decrease somewhat with

further increase in M. If the molecular weight is high, crystallization sets in at a lower elongation, and the ultimate elongation is correspondingly lower. Vulcanizates from polymers of lower molecular weight stretch to high elongations before crystallizing, but rupture before they can be elongated much further. Owing to these competing factors, a maximum occurs if the elongation is decreased by an increase in degree of unsaturation for reasons which are obvious in the light of the earlier discussion of the high-elongation portions of the stress-strain curves.

The effect of carbon black is somewhat obscured by the lack of data bearing on the degree of breakdown which occurs during compounding with carbon black. Solubility data on vulcanizates from low polymers indicate that the degree of cross-linking probably is not markedly affected by carbon black. Nevertheless, tensile strength is developed at considerably lower molecular weights in its presence

This reinforcing effect disappears, as far as tensile strength is concerned, as the molecular weight is increased. At the highest molecular weights the tensile strength is reduced, as compared with the pure-gum cures, by an amount which corresponds roughly to the volume percentage of the pigment. In other words, the strength of the black-loaded vulcanizate is about equivalent to the strength of the Butyl rubber in the vulcanizate, the pigment being considered to contribute nothing. There is no enhancement of tensile strength such as occurs when carbon black is incorporated into natural rubber or other synthetic rubbers. Perhaps this situation is due to the low adhesion between polyisobutylene chains and the carbon black surface.

CREEP IN BUTYL VULCANIZATES

Table XII records typical creep measurements under constant load at 25° C. When relative length α is plotted against the log of time t as in Figure 15, the relationship observed is approximately linear, though not exactly so. Approximate linearity in this type of plot is generally found for creep measurements on rubber[35] and other polymeric materials[36]. The degree of curvature for other samples and at various loads is about the same as for the examples shown in Figure 15. Inasmuch as the curvature is small and reasonably constant, the slope of this plot at 10 minutes has been chosen to express the creep rate.

The creep rate depends in a rather complex manner on the applied load. A better criterion for characterizing a given rubber is afforded by the relaxation

TABLE XII

CREEP OF BUTYL VULCANIZATES AT CONSTANT LOAD

Polymer II-5 (21 lb. per sq. in.)		Polymer II-5 (42 lb. per sq. in.)		Polymer V-2 (44 lb. per sq. in.)	
Time (min.)	$\alpha = L/L_0$	Time (min.)	$\alpha = L/L_0$	Time (min.)	$\alpha = L/L_0$
0.5	1.2265	0.5	1.680	1	1.4746
1	1.2352	1	1.711	2	1.4825
2	1.2421	2	1.738	4	1.4883
4	1.2469	4	1.762	8	1.4939
8	1.2516	8	1.784	15	1.4991
16	1.2581	16	1.808	39	1.5050
32	1.2634	32	1.827	76	1.5094
60	1.2670	64	1.846	100	1.5117
95	1.2688	100	1.857		

constant, representing the rate of decrease in the tension at constant elongation. This quantity can be deduced from the creep rate as follows: We assume that G of Equation 11 is time dependent, and that φ depends only on α. Then at constant load τ:

$$d\tau = \varphi(\partial G/\partial \ln t)_\alpha d \ln t + G(\partial\varphi/\partial\alpha)_t d\alpha = 0$$

which rearranges to

$$(\partial \ln G/\partial \ln t)_\alpha = -(\dot{\varphi}/\varphi)(\partial\alpha/\partial \ln t)_\tau$$

where the derivative of φ with respect to α is written as $\dot{\varphi}$. Assuming φ to be represented approximately by Equation 9, the relaxation "constant" becomes:

$$(\partial \ln G/\partial \ln t)_\alpha = -\left[\frac{\alpha^3 + 2}{\alpha(\alpha^3 - 1)}\right](\partial\alpha/\partial \ln t)_\tau \qquad (25)$$

Table XIII presents values of the relaxation constant computed using this equation, from the slope at $t = 10$ minutes of curves such as those shown in

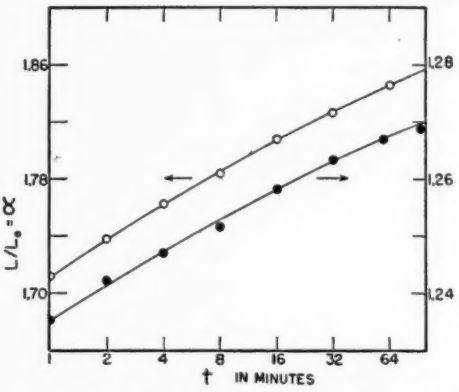


FIG. 15.—Typical creep measurements *vs.* log of time.

Figure 15 and from α at 10 minutes. For a given sample the relaxation "constant" varies somewhat with initial elongation. It increases with increasing α up to about $\alpha = 2$, then decreases as the load is further increased. In general, the values are sufficiently uniform to permit characterization of the sample by an interpolated creep constant at about $\partial = 1.5$ (last column of Table XIII).

When the network is rapidly deformed, terminal chains are distorted into nonrandom configurations, much as are the chains bound at both ends to cross-linkages. Unlike the latter, however, they are able to relax, owing to the fact that one end of each terminal chain is unattached, and are therefore free to "diffuse" to a new (statistically more probable) location. Hence, with the passage of time they rearrange to random configurations, and their contribution to the force of retraction eventually vanishes. If observations are made at constant deformation, relaxation of the stress is observed; if at constant load, creep ensues.

The fraction, or number, of terminal chains for a given degree of cross-linking is approximately proportional to M, or to $\overline{M}_n$ if the polymer is heterogeneous (Equations 9 and 9A). If, in accordance with the previous discussion,

TABLE XIII

SUMMARY OF CREEP RESULTS AT 25° C SHOWING DEPENDENCE OF RELAXATION CONSTANT ON MOLECULAR WEIGHT

Polymer fraction or mixture	$M \times 10^{-3}$ [a]	Ten-minute values: Load, (lb. per sq. in.)	$\alpha = L/L_0$	$\frac{\alpha^3+2}{(\alpha^3-1)\alpha}$	$\left(\frac{d\alpha}{d \ln t}\right)_\tau \times 100$	Relaxation constant $\left(\frac{d \ln b}{d \ln t}\right)_\alpha \times 100$	Interpolated relaxation constant for $\alpha = 1.5$
Low-unsaturation vulcanizates (60-minute cures)							
I-1	1080	21	1.221	3.82	0.31	1.19	1.25
		42	1.630	1.167	1.09	1.27	
		63	2.40	0.514	2.40	1.23	
I-4	650	20	1.224	3.76	0.39	1.47	1.7
		40	1.662	1.10	1.69	1.86	
		60	2.38	0.521	3.30	1.72	
		80	3.56	0.300	4.65	1.40	
II-3	310	21	1.276	2.96	0.72	2.13	2.20
		42	1.881	0.813	2.74	2.23	
II (5.5–6) [b]	275	21	1.254	3.26	0.77	2.50	2.7
		42	1.792	0.910	3.15	2.85	
II-7	202	20	1.329	2.43	1.39	3.38	3.4
		40	2.050	0.680	5.1	3.45	
A-2	300	..	1.595	1.242	2.37	2.94	2.9
D-1	240	..	1.514	1.462	2.26	3.30	3.3
D-2	175	..	1.375	2.09	1.94	4.05	4.05
II-A (unfractionated	200	20	1.315	2.56	1.17	3.00	3.15
		40	2.033	0.692	4.85	3.36	
High-unsaturation vulcanizates (30-minute cures)							
V-1	580	22	1.190	4.52	0.226	1.02	1.05
		44	1.504	1.495	0.70	1.05	
V-2	480	20	1.1925	4.46	0.252	1.12	1.19
		40	1.496	1.525	0.78	1.19	
V-4	280	22	1.2175	3.89	0.38	1.48	1.52
		44	1.644	1.14	1.36	1.55	
V-6	155	22	1.294	2.76	0.80	2.21	2.2
V-7	60	14	1.327	2.45	1.23	3.0	3.5
		22	1.545	1.37	2.72	3.7	

[a] Number-average molecular weights are given for mixtures of fractions and for the unfractionated polymer II-A.
[b] This particular fraction was not included in Table II.

creep in Butyl vulcanizates originates for the most part in terminal chains, the relaxation constant should be expected to increase with $1/M$. In Figure 16 the relaxation constants from the last column of Table XIII are plotted against $1/M$ or $1/\overline{M}_n$ in the case of heterogeneous polymers. The relaxation constant increases about linearly with $1/M$, a plausible result in the light of the previous discussion. In further confirmation of linear dependence of the relaxation constant on the number of terminal chains, heterogeneous polymers fall approximately in line with the results for fractions, number-average molecular weights being employed.

The extrapolated relaxation constants for infinite molecular weight are by no means negligible. Not all of the creep can be attributed to relaxations of terminal chains, of which there are none when M is ∞; some of it evidently arises from rearrangements in the configurations within principal chains.

Although their intercepts are similar, the slope of the curve for the polymers of low unsaturation is about 2.3 times that for the high-unsaturation polymers. If creep depended merely on the proportion of the vulcanizate occurring in terminal chains, irrespective of their average lengths, the slopes of these lines should be in the ratio of the respective M_c values—*i.e.*, about as 1.7 is to 1. Apparently the relaxation constant depends also on the lengths of these chains which are free to relax.

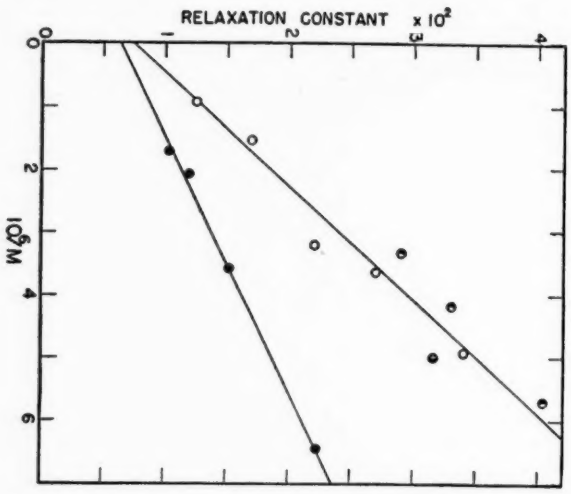


FIG. 16.—Relaxation constant *vs.* reciprocal of molecular weight (pure-gum cures)
○ Low-unsaturation fractions
◐ Mixtures of low-unsaturation fractions
◑ Unfractionated polymer II-A
● High-unsaturation fractions from polymer V

SUMMARY AND CONCLUSIONS

In typical vulcanization of Butyl rubber with sulfur, zinc oxide, and thiuram accelerator, only 1 in about 3 of the diolefin units present is cross-linked. When the same recipe is employed, this efficiency of utilization of diolefin units shows remarkably little variation over a wide range in diolefin content. The Butyl polymers with which most of the experiments were conducted, referred to as low-unsaturation Butyl, contained about 0.5 mole-per cent of diolefin units. About 1 structural unit in 650 was cross-linked during vulcanization of these polymers; the corresponding molecular weight, M_c, per cross-linked unit was about 37,000. Polymers of higher unsaturation (1.0 to 1.2 mole-per cent diolefin) employed in some of the experiments gave vulcanizates in which M_c was 20,000 to 25,000.

Two types of chain elements of the network structure formed by cross-linking the primary Butyl polymer molecules during vulcanization must be distinguished—principal or "active" chains, each of which represents the portion of a molecular chain extending from one cross-linkage to the next, and terminal or "inactive" chains, extending from the end of a primary molecule to the first cross-linkage along its length. The former are permanently oriented by stretching, the latter are not. Hence, only the principal chains contribute

to general elastic properties. Likewise, only the principle chains are encouraged to crystallize when the sample is stretched. The unoriented terminal chains, of which there are two for each primary molecule, consequently are detrimental to strength. Physical properties can be quantitatively interpreted on the basis of this elementary concept of the essential structure of a typical rubber vulcanizate.

In accordance with statistical mechanical theories of rubber elasticity, stress-strain curves for various pure-gum Butyl vulcanizates are found to be similar in shape; up to about 400 per cent elongation, one can be superimposed on another merely by altering the stress scale by a suitable factor. The factor of proportionality, G, expressing the force for a given elongation, depends on structure. According to previous theories, which take no account of network imperfections such as arise from the presence of terminal chains, G should be proportional to the number of chain elements—*i.e.*, inversely proportional to M_c. Consideration of the influence of the finite molecular weight M of the primary molecules (in a more rigorous manner than the approach mentioned in the preceding paragraph might indicate) shows that G, and hence the "modulus" (tension) at a given elongation, should be proportional to

$$(1/M_c)(1 - 2M_c/M)$$

The latter factor represents the correction for network imperfections. The modulus at 300 per cent elongation has been observed to vary linearly with the reciprocal of M when the degree of cross-linking (and hence M_c) is held constant in accordance with this expression. From the slope of this relationship, M_c for the low-unsaturation polymers is estimated to be 37,000, in good agreement with the figure (35,000) estimated from the critical molecular weight for incipient gelation during vulcanization.

While the dependence of modulus on primary molecular weight M (before vulcanization) is in good agreement with theory, the magnitude of the observed modulus is several times greater than that calculated from theory. Furthermore, the modulus extrapolated to $M = \infty$ shows a much smaller change with degree of cross-linking than the direct proportionality to $1/M_c$ predicted by theory. These observations are adequately explained by the assumption of network entanglements which impose additional restrictions on chain configurations.

Equilibrium swelling measurements in cyclohexane closely parallel the results on the force of retraction. Taking the swelling ratio SR to be the volume of the swollen vulcanizate divided by the volume of dry rubber before dilution with solvent, theory predicts that $1/(SR)^{5/3}$ should depend on the structure of the vulcanizate in the same manner as the modulus. This quantity, in analogy with the modulus, has been found to vary linearly with $1/M$. From the slope of this relationship an M_c value of 39,000 has been estimated for vulcanizates from the low unsaturation polymers. As further verification of the predicted similar dependences of swelling and modulus on vulcanizate structure, inverse proportionality between the modulus and the 5/3 power of the swelling ratio has been demonstrated for vulcanizates, regardless of primary molecular weight, molecular-weight heterogeneity, and degree of cross-linking. It is evident that the same cross-linkages are effective, both in the response of the rubber to deformation and in its reaction to swelling. van der Waals forces, therefore, play no part in contributing to the effective degree of cross-linking, and the same entanglements are operative in the swollen rubber as in the elongated, unswollen material.

At elongations above 400 per cent, the precise region depending on the vulcanizate structure, the slope of the stress-strain curve increases rapidly, reaching a high value. Thereafter the curve continues with approximately constant (high) slope to the breaking point. It is in this part of the stress-strain curve that high tension is developed, and hence the ultimate strength is determined by the character of the rubber in this region.

The fairly abrupt rise in the stress-strain curve is believed to coincide with the occurrence of crystallization; over the final steep portion of the stress-strain curve the rubber is considered to be predominantly crystalline. An increase in degree of cross-linking (decrease in M_c) causes crystallization to set in at a lower elongation, presumably owing to the greater alignment of the chains for a given elongation. A decrease in molecular weight M postpones the onset of crystallization toward higher elongations, owing to the increase in the proportion of nonoriented terminal chains which act as a diluent on the remainder of the structure.

Tensile strength ordinarily has been considered to be a most intractable property from a theoretical viewpoint. The results obtained with Butyl, however, are consistent with an unexpectedly simple structural interpretation: The tensile strength is a linear function of the fraction of the structure which is oriented by stretching. The tensile strength is presumed to depend directly on the degree of crystallinity achieved at high elongations. This will depend on the percentage of the material which is oriented by stretching.

Thus, the dependence of tensile strength on structure can be expressed:

$$TS = a(w_A - b) \tag{26}$$

where a and b are constants, and the weight fraction w_A of active network, in the absence of diluents, is given by

$$w_A = 1 - 2M_c/(M + M_c)$$

In accordance with the above generalization, the tensile strength at fixed degree of cross-linking (constant M_c) varies linearly with $1/(M + M_c)$; alternatively, within experimental error the tensile strength is linear with $1/M$, M being $>> M_c$ over the significant range. The extrapolated tensile strength (25° C) for infinite molecular weight ($w_A = 1$) is about 5600 pounds per square inch. The linear relationship with w_A extrapolates to zero strength when w_A is 0.4, although it is actually invalid below about 100 pounds per square inch; vulcanizates with such low strengths show no evidence of crystallization on stretching (before they fail), and presumably rupture occurs by a different mechanism.

The same linear relationship between TS and w_A appears to hold when M_c is varied by altering the proportion of diolefin in the polymer, provided it is not too high. The onset of appreciable tensile strength occurs when there are an average of about 3 cross-linked units per molecule, regardless of the lengths of the molecules. If the percentage of diolefin units is greater than about 1.0, the tensile strength when the molecular weight is large is depressed, owing, apparently, to the inability of the diolefin unit to fit into the polyisobutylene crystal lattice.

As further evidence for the generality of Equation 26, it is found to apply (with the same values of a and b) to vulcanizates which contain inert diluents not connected to the network, such as polyisobutylene or mineral oil; it is necessary in this case merely to let w_A represent the weight fraction of active network in the composition consisting of vulcanized Butyl and diluent. In

other words, the diluent and terminal chains are quantitatively equivalent in their effects on tensile strength.

Relaxation rate constants have been computed from creep measurements on the Butyl vulcanizates. These also are approximately linear functions of $1/M$ when M_c is constant. The results extrapolate to appreciable, though small, relaxation rates for $M = \infty$. It has been concluded that most, but not all, of the relaxation (or creep) originates in rearrangements in the configurations of the terminal chains.

Heterogeneous polymers exhibit properties which in all cases coincide with those of a fraction for which M is equal to the number-average molecular weight $\overline{M}_n$ of the heterogeneous polymer. In other words, in each of the various relationships derived from experiments on vulcanized fractions it is necessary merely to replace M with $\overline{M}_n$ when dealing with heterogeneous polymers. This explicit dependence on number-average molecular weight agrees with expectations based on theoretical considerations, according to which each of the various properties depends on the number of terminal chains or on the number of primary molecules.

Although the experiments reported here have been confined to Butyl rubber, it is felt that similar relationships pertaining to "modulus", swelling capacity, and creep can be expected to apply to other vulcanized rubberlike materials. The tensile strength of Butyl, on the other hand, appears to be intimately related to the development of a high degree of crystallinity on stretching. In rubbers such as GR-S which do not possess this characteristic, there is no reason to anticipate that the tensile strength will vary linearly with w_A. A similar linear relationship probably would be expected to apply to natural rubber, however.

Finally it should be admitted that many of the measurements conducted in this investigation leave much to be desired from the standpoint of accuracy. With the application of more refined techniques, deviations from some of the relationships suggested by the present results probably will be observed. Some of these relationships may be presumed to represent first approximations only. At any rate, the results which have been secured justify the view that properties of rubberlike materials can be interpreted rationally and simply in terms of their structures.

ACKNOWLEDGMENT

The writer wishes to acknowledge the assistance of Edward Krieg, Jr., A. F. Sayko, and S. B. Robison in carrying out the fractionations, compounding, curing, and testing work, and of Elinor F. Moreton who conducted most of the swelling measurements. He is also indebted to W. J. Sparks, R. M. Thomas, and their associates for furnishing the desired range of Butyl polymers, and to John Rehner, Jr., for assistance in devising the methods of compounding.

SUMMARY

The investigation was undertaken in an attempt to establish the fundamental connections between the physical properties of a typical vulcanized rubberlike polymer and its chemical structure. The structural variables to be considered are the molecular weight of the "primary molecules" entering the vulcanizate, their molecular-weight distribution, and the concentration (or frequency) of cross-linkages introduced during vulcanization. The molecular weights of Butyl rubbers were determined by previously established procedures;

the effects of molecular-weight heterogeneity were suppressed by careful fractionation from very dilute solution. An indirect method, based on the theory of gelation and on the observation of critical molecular weight for incipient gelation (partial insolubility) in "vulcanizates" formed when the cross-linking capacity is fixed, was employed to determine the frequency of occurrence of cross-linked units—a quantity not hitherto evaluated in a vulcanized rubber. In representative pure-gum vulcanizates of Butyl the molecular weight per cross-linked unit ranges from about 35,000 to 20,000, depending (inversely) on the diolefin content of the raw rubber. Micro compounding and testing procedures have been devised for evaluating the necessarily small samples obtained in fractionation. Complete evaluation of tensile strength, stress-strain characteristics, swelling in solvents, and creep rate can be obtained with as little as 3 grams of rubber. Results are no less reproducible than those obtained with conventional procedures requiring 50 grams or more. A number of relationships between vulcanizate structure and physical properties have been established. The feasibility of a rational approach to the interpretation of properties of rubber vulcanizates in terms of molecular structure has been demonstrated.

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TENSILE STRENGTH IN RELATION TO MOLECULAR WEIGHT OF HIGH POLYMERS *

PAUL J. FLORY

RESEARCH LABORATORY, GOODYEAR TIRE AND RUBBER CO., AKRON, OHIO

Sookne and Harris[1] have shown recently that the tensile strength of cellulose acetate depends explicitly on the *number average* molecular weight, regardless of the molecular weight distribution. They have found also that the tensile strength (and other mechanical properties as well) of a "blend" composed of a mixture of cellulose acetate fractions equals the *weight average* of the tensile strengths of the components, *i.e.*:

$$T_m = \sum_i w_i T_i \tag{1}$$

where w_i is the weight fraction of the component which by itself exhibits a tensile strength T_i and T_m is the tensile strength of the mixture. These seemingly incongruous statements can be reconciled only if the tensile strength-molecular weight relationship assumes a particular form, as will be shown below. In other words, these statements actually define the form of the relationship of tensile strength to molecular weight. This same relationship also applies to Butyl rubber vulcanizates, and, hence, may be quite general.

Let the tensile strength be expressed as a function of $1/M$. Then:

$$T = f(1/M) = a_0 + a_1/M + a_2/M^2 + \cdots \tag{2}$$

where a_0, a_1, etc., are numerical coefficients in the series expansion of $f(1/M)$. According to the first stated characteristic of this function, the tensile strength of a mixture of cellulose acetate molecules differing in size is given by:

$$T_m = f(1/\bar{M}_n) \tag{3}$$

where $\bar{M}_n$ is the number average molecular weight for the mixture. By definition:

$$1/\bar{M}_n = \sum_i (w_i/M_i)$$

where M_i is the molecular weight of the i-th species. Hence:

$$T_m = f(\sum_i w_i/M_i)$$

Employing the series expansion of Equation (2):

$$T_m = a_0 + a_1 \sum_i (w_i/M_i) + a_2 (\sum_i (w_i/M_i))^2 + \cdots \tag{4}$$

* Reprinted from the *Journal of the American Chemical Society*, Vol. 67, No. 11, pages 2048–2050, November 1945.

Additivity of tensile strength according to the weight fractions of the components, as expressed by Equation (1), requires that:

$$T_m = \Sigma w_i f(1/M_i) = a_0 + a_1 \sum_i (w_i/M_i) + a_2 \Sigma(w_i/M_i^2) + \cdots \quad (5)$$

The first two terms of Equations (4) and (5) are identical, but higher terms differ. Consequently, the two characteristics of the dependence of tensile strength on molecular weight of cellulose acetate observed by Sookne and Harris are consistent only when a_2 and higher coefficients in Equation (2) are equal to zero. The relationship then assumes the simple form:

$$T = a_0 + a_1/M \quad (6)$$

in which M is to be replaced by the number average $\bar{M}_n$ when dealing with heterogeneous polymers. The same analysis can be applied to other properties which likewise seem to depend on the number average molecular weight and to exhibit additivity in their weight fractions[1].

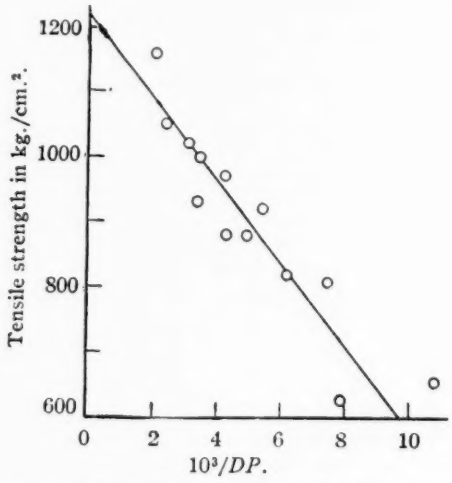

FIG. 1.—Tensile strength *vs.* reciprocal of chain-length for cellulose acetate fractions. The data are those of Sookne and Harris[1].

In the accompanying figure Sookne and Harris' tensile strength values for fractions are plotted against the reciprocals of their degrees of polymerization determined by the osmotic pressure method. The relationship is linear within experimental error, in agreement with Equation (6), as necessarily must be the case in view of their observations stated in the first paragraph above. A similar dependence of tensile strength on molecular weight (before vulcanization) has been observed for Butyl rubber vulcanizates[2] when the concentration of cross-linkages is held constant.

It is rather surprising that this similarity exists between two materials so fundamentally different in properties and structure. Vulcanized Butyl rubber possesses a network structure owing to the cross-linkages between occasional units of the primary polymer molecules (one cross-linked unit for each 300 or more units); there are no cross-linkages in cellulose acetate. The latter is normally crystalline, and elongates only some 25 per cent at break; the former

stretches to ten or more times its initial length and crystallizes only when stretched. The only evident features in common are their predominantly linear polymeric structures and the occurrence in each of them of high degrees of crystallinity when subjected to severe tension.

The dependence of the tensile strength of Butyl rubber on its structure can be stated more generally: the tensile strength appears to be a *linear function of the percentage of the structure permanently oriented by stretching* over a wide range of structural variations. Within the network structure only "chains" (portions of the rubber molecules) extending from one cross-linkage to another are permanently oriented by stretching; chains reaching from the end of a primary molecule to the first cross-linkage along its length are not permanently distorted by a deformation of the sample. The latter, therefore, generally does not undergo crystallization, but rather acts like diluents dispersed in the oriented portion of the network.

Equation (6) can be deduced as a special case of the more general dependence stated in *italics* above. If the concentration of cross-linkages (degree of vulcanization) is fixed, the percentage of the rubber occurring in nonorienting terminal chains is inversely proportional to M, the molecular weight of the primary molecules (*i.e.*, the molecular weight of the rubber molecules before vulcanization). Hence, in accordance with the above generalization, the tensile strength varies linearly with $1/M$ at constant degree of cross-linking.

This interpretation of the tensile strength-molecular weight relationship cannot be applied to cellulose acetate, which has no primary valence network. It would appear that the similar dependence on molecular weight in this case is to be regarded as coincidental rather than as an indication of identical structural behavior when subjected to severe stresses. In this connection Spurlin[3] has suggested that rupture originates at the ends of molecules and, hence, that the ease of failure (conversely the strength) should depend on the number of ends of molecules. This will explain the explicit dependence of strength on the number average molecular weight; it does not seem to offer a satisfactory basis for linear dependence on $1/M$, or $1/\bar{M}_n$, however.

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A STUDY OF THE VARIOUS MOLECULAR FRACTIONS OF RUBBER AND THEIR BEHAVIOR DURING VULCANIZATION *

E. A. HAUSER

DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

D. S. LE BEAU

MIDWEST RUBBER RECLAIMING CO., EAST ST. LOUIS, MISSOURI

AND

YEN SHEN

BAKELITE CORPORATION, BOUND BROOK, NEW JERSEY

During the last twenty-five years considerable work has been carried out to determine, by physical or chemical means, the structure of natural rubber. Freundlich and Hauser[1] were the first to prove with the use of a micromanipulator that the individual rubber particle in Hevea latex consists of a viscous interior, surrounded by a tough, elastic skin. The first to discover the effect of different solvents on rubber were Feuchter[2] and Pummerer[3]. Since then fractionation of high polymers has become a standard procedure for their evaluation. The present investigation was carried out to study in somewhat greater detail the fractionation of prime Hevea ribbed smoked sheet and also the vulcanization characteristics of each fraction and its contribution to the physical properties of the total rubber.

Several methods for the fractionation of rubber are known. However, since large amounts of each fraction were needed for the purpose of this investigation, fractionation was carried out by the diffusion method. Viscosities were determined by the use of an Ostwald viscometer, and molecular weights were calculated by the Staudinger and Arrhenius equations. Although Arrhenius' equation[4] has hardly any theoretical basis, it proved to be subject to fewer discrepancies than Staudinger's equation[5] when using solutions of different viscosity levels. Kemp[5] has shown that the variations of η_{sp}/c are—contrary to Staudinger's claim—quite considerable. The slope of η_{sp}/c, if plotted against η_{sp} is more pronounced the higher the molecular weight of the polymer under investigation; whereas, the slope of $\log_{10} \eta_r/c$, if plotted against η_r, is small over a fairly wide range of viscosities. Therefore, the calculations of the molecular weight were carried out preferentially by the use of Arrhenius' equation.

Since fractionation within narrow molecular weight ranges is extremely difficult, Kemp's suggestion[6] for the use of a socalled poor solvent rather than a good solvent was accepted, and the fractionation was carried out by diffusion

* Reprinted from *The Rubber Age* (New York), Vol. 58, No. 1, pages 59–65, October 1945.

in hexane (b.p. 60–70° C). The choice of a poor solvent unquestionably decreases the speed of fractionation, as the swelling of the rubber is decreased, but it equally would give greater assurance against the presence of discrete particles of rubber which—in a good solvent—may easily become detached from the insoluble part of the rubber and dispersed in the solution, thereby influencing any determinations of viscosity as well as the percentage of rubber extracted for any given time of fractionation.

The viscosity of each fraction was determined in benzene as well as in hexane, whereupon the constant for hexane was calculated.

PROCEDURE

Smoked sheet rubber was first cleaned of any dirt adhering to the outside of the sheets and then dried under vacuum. It was cut into small pieces, placed in a cheesecloth bag (which had previously been subjected to both acetone and hexane extraction) and extracted in acetone for 72 hours at room temperature. The rubber was then placed in a vacuum desiccator to remove traces of acetone. After this actual fractionation was begun by immersion in hexane. During acetone extraction and fractionation, the air above the liquid was replaced by carbon dioxide, and the container was stored in the dark (temperature of fractionation 22–24° C). The solution of rubber resulting from each fractionation was carefully decanted, avoiding disturbance of the rubber remaining in the bag as much as possible. To avoid oxidation of the rubber in solution which might occur during unduly prolonged storage of the solution, the viscosity measurements in hexane were carried out immediately after removal of the solution. If it was necessary to recover the rubber from the solution, this was done as soon as possible by placing the solution to which 1 per cent of sym. di-β-naphthyl-p-phenylenediamine had been added in a vacuum-distillation apparatus. To remove the solvent as quickly as possible, the rubber solution was kept at room temperature during evacuation by means of a water bath. After all solvent had been removed, the thin sheet of rubber was placed in a vacuum desiccator in a dark place. The gel rubber was recovered in small batches in the same way.

The accompanying tables show the rubber extracted, η/η_0 in hexane and benzene for various concentrations of rubber, the molecular weights as calculated by Staudinger's as well as Arrhenius' equation, and the ratio of the molecular weights obtained for each fraction in hexane and benzene.

The second run of fractionations as recorded in Table II was carried out to study a wider range of molecular weights and thereby to determine more accurately the ratio of the calculated molecular weights obtained from benzene and hexane solutions. This difference has already been noticed by Kemp[6], and it may be attributed to the effect of the solvent on the rubber. It is well known that rubber swells to different degrees in various solvents[7]. Solubility depends on the specific affinity of the solvent for the solute. Thus the rubber molecule may have greater affinity for one solvent than for another.

Adjacent rubber chains are bound together firmly by cohesive forces, but purely mechanical entanglement of the long chains also must be taken into consideration. A solvent with high specific affinity for the rubber chains is capable of penetrating the structure, at the same time solvating the chains and prying them apart. The so-called bound volume of solvent, *i.e.*, that part of the solvent which becomes firmly adsorbed on the rubber chains, varies with the particular solvent.

TABLE I

VISCOSITY MOLECULAR WEIGHT OF SMOKED
(Sample used—50 grams; acetone-

Number of fractions	Percentage extracted (%)	Accumulative percentage extracted (%)	η/η_0 in hexane solution at 0.1C	0.2C	0.3C	M.W. (M) determined in hexane solution at 0.1C	0.2C	0.3C
1st	8.35	8.35	53.4/45.4	62.25/45.4	71.9/45.4	87,900* 80,600**	93,300* 78,000**	97,200* 75,600**
2nd	4.74	13.09	54.7/45.4	65.5/45.4	77.4/45.4	108,700* 96,700**	117,500* 95,100**	124,700* 92,300**
3rd	6.95	20.04	55.4/45.4	67.6/45.4	81.4/45.4	129,300* 114,000**	143,600* 114,000**	155,200* 111,700**
4th	4.99	25.03	54.8/45.4	65.95/45.4	79.4/45.4	150,400* 133,600**	164,400* 132,500**	181,300* 132,300**

TABLE II

VISCOSITY MOLECULAR WEIGHT OF SMOKED
(Sample used—60 grams; acetone-

Number of fractions	Percentage extracted (%)	Accumulative percentage extracted (%)	η/η_0 in hexane solution at 0.1C	0.2C	0.3C	M.W. (M) determined in hexane solution at 0.1C	0.2C	0.3C
1st	15.20	15.20	52.9/47.1	59.15/47.1	66.5/47.1	91,800* 83,500**	95,400* 81,900**	102,400* 82,700**
2nd	11.13	26.33	52.75/47.1	59.4/47.1	66.75/47.1	113,800* 107,500**	123,800* 107,500**	131,900* 108,600**
3rd	7.83	34.16	51.2/47.1	55.7/47.1	60.9/47.1	124,100* 116,300**	130,100* 116,800**	139,200* 119,400**
4th	4.81	38.97	....	52.3/47.1	55.25/47.1	....	129,900* 120,400**	135,800* 122,300**
5th	5.69	44.66	....	....	....	....	....	....
6th	3.40	48.06	....	53.45/47.1	57.15/47.1	....	149,800* 137,300**	158,100* 140,000**

* M.W. calculated from Staudinger equation: $M = \dfrac{\eta/\eta_0 - 1}{3 \times 10^{-4} \times \dfrac{c}{68}}$

c = concn. of solution in g. per liter

Finally, individual fragments of the rubber are carried into the solution. The fragments can be molecules or they can be incompletely disintegrated aggregates of rubber. A socalled good solvent usually shows greater swelling power than a poor solvent. Therefore, the danger of the presence of incompletely dissolved rubber aggregates in the solution is greater in a good solvent. Since any kind of agitation was rigorously avoided during fractionation, such aggregates may take a long time to disperse. It is well known that the particle size of any colloidal dispersion affects the viscosity of the dispersion to a great extent[8]. Therefore, in determining the molecular weight of rubber by the viscosity of its solution, we must remember that not only the chain length of the molecules has to be taken into consideration, but also their state of dispersion. This may cause the differences in the calculated molecular weight for different solvents not accounted for by any of the equations.

SHEET FRACTIONS IN DIFFERENT SOLVENTS
soluble substances—2.70 per cent)

η/η_0 in benzene solution at			M.W. (M′) determined in benzene solution at			Ratio of M′ to M at		
0.1C	0.2C	0.3C	0.1C	0.2C	0.3C	0.1C	0.2C	0.3C
85.8/68.8	105.8/68.8	128.8/68.8	123,400*	134,300*	144,100*	1.40	1.45	1.49
			112,000**	105,000**	101,000**	...	1.34	1.33
89.2/68.8	111.75/68.8	140.9/68.8	157,400*	165,700*	185,400*	1.45	1.41	1.48
			127,800**	125,400**	124,200**	1.32	1.32	1.34
89.5/68.8	115.7/68.8	147.8/68.8	176,700*	200,100*	224,700*	1.37	1.39	1.45
			151,000**	149,400**	143,000**	1.32	1.31	1.29
86.6/68.8	110.0/68.8	136.5/68.8	187,900*	217,500*	238,300*	1.25	1.32	1.31
			171,600**	169,000**	153,000**	1.28	1.28	...

SHEET FRACTIONS IN DIFFERENT SOLVENTS
soluble substances—2.96 per cent)

η/η_0 in benzene solution at			M.W. (M′) determined in benzene solution at			Ratio of M′ to M at		
0.1C	0.2C	0.3C	0.1C	0.2C	0.3C	0.1C	0.2C	0.3C
79.95/68.8	92.4/68.8	106.95/68.8	120,800*	127,900*	137,800*	1.31	1.34	1.35
			108,700**	105,300**	105,400**	1.30	1.29	1.28
80.05/68.8	82.7/68.8	106.9/68.8	155,100*	164,700*	175,000*	1.36	1.33	1.33
			140,300**	137,000**	136,100**	1.30	1.27	1.25
77.1/68.8	86.0/68.8	95.6/68.8	172,000*	178,200*	185,100*	1.39	1.37	1.33
			158,700**	155,400**	152,800**	1.36	1.33	1.29
....	78.4/68.75	83.6/68.75	....	169,500*	169,500*	...	1.30	1.25
			....	151,000**	150,000**	...	1.26	1.23
....	82.25/68.75	90.3/68.75	....	195,500*	208,100*	...	...	...
			....	174,500**	176,900**	...	...	...
....	80.2/68.75	87.7/68.75	....	185,000*	204,200*	...	1.24	1.29
			....	167,300**	176,200**	...	1.22	1.26

** M.W. calculated from Arrhenius equation: $M = \frac{0.75 \times 10^4 \log_{10} \eta/\eta_0}{\frac{c}{68}}$

c = conc. of solution in g. per liter

Since exact knowledge of the actual structure of the solution is not at hand, a truly conclusive picture of the phenomenon cannot yet be offered. Therefore any introduction of a new constant—covering the effect of the solvent—into either molecular weight equation seems premature.

Tables I and II show very clearly the comparatively small effect the concentration of the solution exerts if the molecular weight is calculated by Arrhenius' equation.

To study the reproducibility of the fractionation, ten separate batches were run. Although the smoked sheet used in this study was designated as prime 1A, some variation in the color of the individual sheets could be noticed, and it was found in general that the darker the color of the sheet, the higher the content of hexane-insoluble gel (Table III).

Figure 1 shows the rate of extraction (per cent per hour) obtained by averag-

TABLE III

FRACTIONATION OF SMOKED SHEET

(Average acetone soluble substances—2.70 per cent)

Batch Number	Sol Rubber: 1st fraction (%)	2nd fraction (%)	3rd fraction (%)	4th fraction (%)	5th fraction (%)	6th fraction (%)	7th fraction (%)	Gel Rubber (%)	Total (%)	Remarks
1	10.84	10.36	10.53	7.78	10.34	5.90	3.80	37.80	100.05	light, transparent sheet
2	10.37	17.36	14.15	9.00	7.00	3.90	2.64	33.30	100.42	light, transparent sheet
3	7.44	9.66	7.62	6.88	9.75	5.85	4.23	46.75	100.78	dark colored sheet
4	13.01	12.00	7.20	4.83	6.24	3.67	2.53	..	..	dark colored sheet
5	10.97	9.73	7.28	5.10	6.91	4.53	3.25	50.40	100.87	dark colored sheet
6	10.20	10.67	7.63	5.38	6.11	4.27	3.82	48.87	99.65	dark colored sheet
7	10.35	9.05	7.94	5.54	10.03	5.00	2.88	..	..	very thick sheet
8	10.15	12.01	9.30	6.60	6.46	4.18	2.77	44.69	98.86	very thick sheet
9	10.50	12.61	10.58	6.80	5.98	3.28	2.44	45.78	100.67	very thick sheet
10	10.00	10.91	..	..	..	..	..	..	..	dark colored sheet
Average	10.37	11.63	8.96	6.27	7.31	4.33	3.07			

ing the percentage extracts for each fraction of all ten batches. The increasing rate of extraction during the first two days is not surprising. First the molecules located in the surface solvate; only thereafter does diffusion of solvated molecules take place from the interior to the surface. This tends to slow down the process of extraction. However, the shape of this curve cannot be regarded as general, since the surface of the rubber exposed to extraction greatly affects the result.

Although during prolonged extraction the slope of the extraction curve decreased very much, it did not reach zero. Therefore, it was thought possible that a breakdown of the molecules might occur during extraction. To verify this point, a total rubber was synthesized from the various fractions in the proportions as found in the original smoked sheet. This rubber was then compounded, vulcanized, and compared in its physical and chemical properties

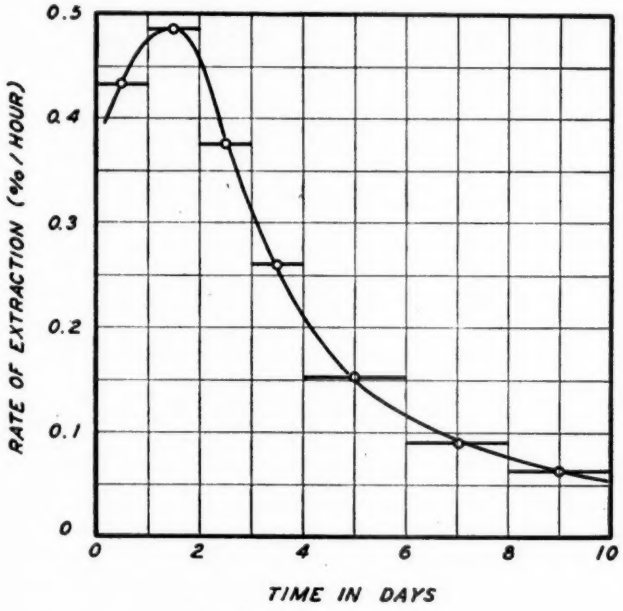

FIG. 1.—Rate *vs.* time of extraction.

with the original. The following compound was used for this purpose as well as throughout the remainder of this investigation:

Rubber	100
Sulfur	3
Zinc oxide	5
Mercaptobenzothiazole	1
Stearic acid	3
Agerite White	1

Mill temperature: 130° F.
Vulcanizing temperature: 270° F.

Since in all cases the fractions of total rubber to be compounded had undergone exhaustive acetone extraction, it was considered of advantage to increase the amount of stearic acid to replenish the natural fatty acids originally present

in the rubber. Figure 2 shows the physical properties of both the original, not fractionated, smoked sheet and the total rubber synthesized from the various fractions in proportions equaling those found in the original. Very little difference in the physical properties of both can be found, and therefore one can conclude that no serious breakdown of the rubber molecules occurred during fractionation. The modulus of the original rubber is slightly higher than that of the synthesized rubber.

There appears to be, however, some retardation of cure in the synthesized rubber. The elongation of the synthesized rubber at undercures and at optimum cure is also somewhat higher than that of the original. This may be accounted for by the following consideration. During fractionation, which is based on the solvation of the lower molecular weight part, the cohesive forces acting between these molecules lose their effectiveness. Besides this, the mechanical entanglement of the molecules is loosened.

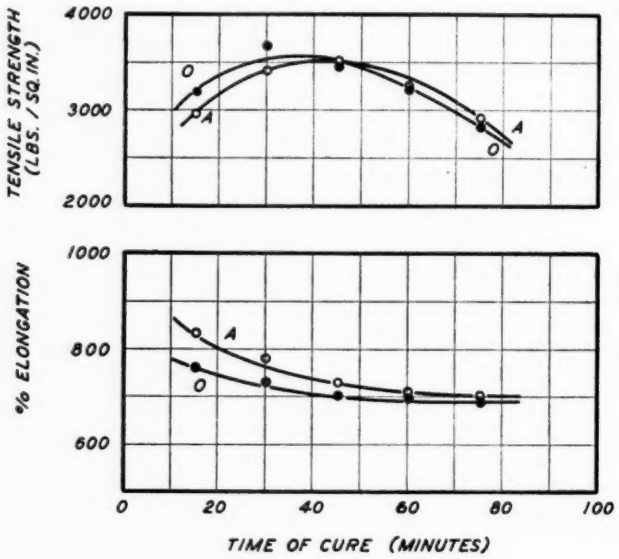

FIG. 2.—Tensile strength and elongation *vs.* time of cure for synthesized total rubber (*A*) and acetone-extracted smoked sheet (*O*).

It is known that rubber stored for a long period at room temperature or chilled exhibits an x-ray diffraction pattern typical for crystals in random arrangement. But if stretched, a typical fiber pattern results, which indicates that the crystallites have now been oriented in the direction of elongation[9].

It is also known that rubber stretched very slowly shows no x-ray diffraction pattern up to an elongation of 500 per cent. This can be explained by assuming that plastic flow takes place, avoiding alignment and orientation of the molecules. The higher the temperature and the slower the rate of elongation, the smaller is the chance for alignment[9]. Besides this, solvation loosens the secondary valence bond between the entangled molecules and permits removal of the lower weight fractions. These are composed of the short chains of the polymer which are dispersed throughout the network made up by the long

chains. Furthermore, the short chains are not held together by secondary forces to the extent that localized alignment results as with the long chains. This is evidenced by the fact that the gel fraction gives a very clear x-ray diffraction pattern, whereas the sol fraction shows no evidence of molecular orientation, even when stretched. That the rubber recovered from these fractions exhibits differences in some of its physical properties can now be readily understood on the basis of these considerations.

The various fractions were analyzed for unsaturation[10], ash, and protein content. The latter two analyses were carried out to determine if and to what extent these components might affect the results. From Table IV it can be

TABLE IV

COMPOSITION OF SMOKED SHEET FRACTIONS
(Average acetone soluble substances—2.70%)

	Number of fraction	Percentage of the total	Percentage of unsaturation	Ash content	Protein content * (%)	Percentage of pure hydrocarbon	Percentage of unsaturation based upon pure hydrocarbon
Sol Rubber	1st	10.37	97.9	0.01	Trace	99.99	97.8
	2nd	11.63	98.3	0.01	Trace	99.99	98.3
	3rd	8.96	98.7	0.02	Trace	99.98	98.7
	4th	6.27	98.3	0.02	Trace	99.98	98.3
	5th	7.31	98.3	0.02	Trace	99.98	98.3
	6th	4.33	98.3	0.02	Trace	99.98	98.3
	7th	3.07	98.9	0.02	Trace	99.98	98.9
Gel Rubber		45.36	93.4	0.45	4.62	94.93	98.5

* % of Protein = % of Nitrogen × 6.5.

seen that the main portion of the ash as well as of the protein remain in the gel rubber. If the values obtained for unsaturation are corrected for the pure rubber hydrocarbon in the sample, hardly any difference in unsaturation for all fractions, including the gel rubber, can be noticed. This indicates that gel rubber consists of long chains of polyisoprene, and that branching—if existing at all—does not occur in the gel to any greater extent than in the sol rubber. (For the calculation of the percentage protein the assumption was made that all nitrogen containing compounds in the rubber consist of protein. If, however, the nitrogen-containing compounds are considered to be glucoproteins and are calculated as such, the percentage unsaturation recalculated on the basis of the pure rubber hydrocarbon exceeds 100 per cent).

The elimination of protein in the rubber is very difficult, and may lead to a degradation of the original hydrocarbon molecules. Therefore, it was considered better to analyze each fraction for its nitrogen content rather than to remove the nitrogen-containing matter.

Since the various amounts of rubber obtained from the ten fractions were too small for proper compounding, several of the fractions were mixed together to form a low molecular-weight sol rubber (up to 125,000) and a high molecular-weight sol rubber (130,000–170,000). These two batches, the gel rubber, and a batch synthesized from the various fractions according to the original proportions as present in smoked sheet, were compounded, tested for their physical properties, and chemically analyzed. Figures 3 and 4 record the physical properties of these compounds, and Table V its chemical analysis.

It can be seen that the rates of cure of the gel rubber and of the synthesized total rubber are very much faster than that of the two compounds prepared from sol rubber. However we have to bear in mind that the first two contain the nitrogenous matter, whereas the latter two are practically free from these. Beadle and Stevens[11] studied the effect of protein on vulcanization, and found that these substances are responsible for a considerable acceleration of cure.

Although the rate of combination of sulfur cannot be considered as a criterion of vulcanization, it nevertheless is interesting to note that the two compounds prepared from sol rubber and containing only extremely small amounts of proteins show the same and a rather constant rate; whereas the compound prepared from gel rubber (containing the greatest amount of protein) shows an

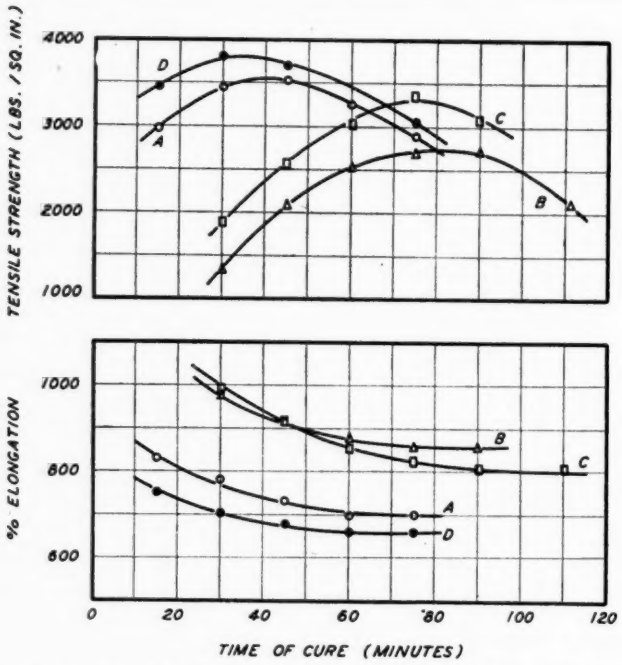

FIG. 3.—Tensile strength and elongation *vs.* time of cure of total rubber (*A*), low molecular-weight sol rubber (*B*), high molecular-weight sol rubber (*C*), and gel rubber (*D*).

appreciable hourly rate of combination, particularly in the very early stages of cure (Figure 5). The synthesized total rubber is very similar in this respect, but the initial rate of sulfur combination is somewhat smaller. At the same time it is rather interesting to note that ΔU at optimum cure is smallest for the gel rubber.

Figures 6, 7, 8, and 9 show the atoms of sulfur combined per double bond for each of the four compounds. Whereas for the synthesized total rubber as well as the two sol rubbers the atoms of sulfur combined per double bond are either between 1 and 2 or close to either 1 or 2, the gel rubber shows a combination of approximately 3 or more atoms of sulfur combined per double bond. Even if proteins accelerate vulcanization, it is hardly plausible to assume that

these proteins promote a combination of 3 atoms of sulfur per double bond. Therefore we must look for another explanation of the phenomenon.

In gel rubber we are dealing with very long and entangled rubber chains. Slippage of the chains is less easy than in sol rubber, and this by itself accounts for higher tensile strength, higher modulus and lower elongation. If, as a result of vulcanization, sulfur bridges are introduced, the length of the chains is theoretically somewhat lengthened, more network is formed, and this causes further difficulties in chain slippage. If sulfur bridges are introduced into sol rubber, they lengthen the chains, but not to such an extent as to impair slippage. The tensile strength increases. The combined sulfur is determined as the difference between total and free sulfur.

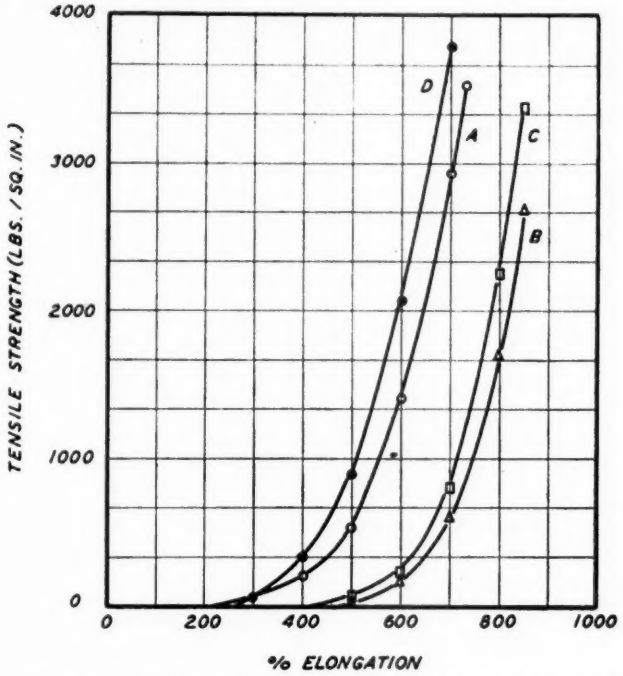

FIG. 4.—Stress-strain relationship of total rubber cured for 45 minutes (*A*), low molecular-weight sol rubber cured for 75 minutes (*B*), high molecular-weight sol rubber cured for 75 minutes (*C*), gel rubber cured for 30 minutes (*D*).

Conceivably it is easier to obtain access to the free sulfur in the sol rubber than in the gel rubber. Neither of the determinations of free sulfur, whether by acetone extraction of the rubber or by the sodium sulfite method (ASTM), relies on the complete solution of the rubber sample. Neither acetone nor sodium sulfite swell rubber to any appreciable extent. Thus it is possible that in extreme cases, as in gel rubber, part of the free sulfur is so tightly occluded into the rubber network that it may not be removed completely. This, of course, would account for a high figure in combined sulfur and, therefore, a high figure in atoms of sulfur per double bond.

In synthesized total rubber we have gel rubber mixed with sol rubber, and removal of free sulfur should be easier. If protein in gel rubber promotes the combination of three atoms of sulfur per double bond, we should expect to

TABLE V

CHEMICAL PROPERTIES OF SMOKED SHEET FRACTIONS
(Temperature of vulcanization—270° F)

Sample	Time of vulcanization (min.)	Total sulfur (%)	Free sulfur (%)	Combined sulfur (%)	Iodine value	Unsaturation (%)
A (total rubber)	0	2.97	2.97	.0	357.0	95.8
	15	2.97	1.82	1.15	347.9	93.3
	30	2.96	1.14	1.82	347.3	93.1
	45	3.00	0.43	2.57	346.4	92.9
	60	2.99	0.15	2.84	347.3	93.15
	75	2.99	0.09	2.90	347.8	93.3
B (low m.w. sol rubber)	0	2.96	2.96	.0	365.8	98.1
	15	2.96	2.63	0.32	..	..
	30	2.96	2.22	0.74	362.0	97.1
	45	2.96	1.87	1.09	360.8	96.7
	60	2.97	1.34	1.63	359.7	96.45
	75	2.98	1.28	1.70	360.0	96.5
	90	3.00	0.84	2.16	359.3	96.4
	110	2.99	0.60	2.39	360.7	96.7
C (high m.w. sol rubber)	0	2.96	2.96	.0	367.2	98.5
	30	2.96	2.22	0.74	362.9	97.3
	45	2.95	1.85	1.10	360.3	96.6
	60	2.96	1.70	1.26	360.7	96.7
	75	2.97	1.06	1.91	360.3	96.6
	90	2.98	0.76	2.22	360.3	96.6
	110	2.97	0.58	2.39	360.6	96.7
D (gel rubber)	0	3.05	3.05	.0	348.3	93.4
	15	3.04	1.58	1.46	344.2	92.3
	30	3.02	0.77	2.25	343.2	92.0
	45	3.05	0.22	2.83	342.3	91.8
	60	3.05	0.09	2.96	342.1	91.8
	75	3.04	0.02	3.02	344.1	92.2

see the effect of it at least to a proportionate extent in synthesized total rubber, where optimum curing times are closer to gel rubber than to those of sol rubber, and, therefore, any loss in unsaturation due to heat[12] could be disregarded. This, then, brings up the question as to whether the nitrogenous compounds in gel rubber can be considered as vulcanization accelerators, or whether the effect noticed is not due to the structure of the gel itself.

It should be pointed out that Beadle and Stevens[11] based their deductions

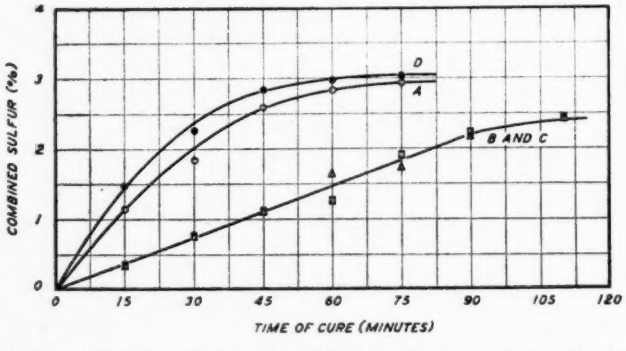

FIG. 5.—Combined sulfur *vs.* time of cure for total rubber (*A*), low and high molecular-weight sol rubber (*B* and *C*) and gel rubber (*D*).

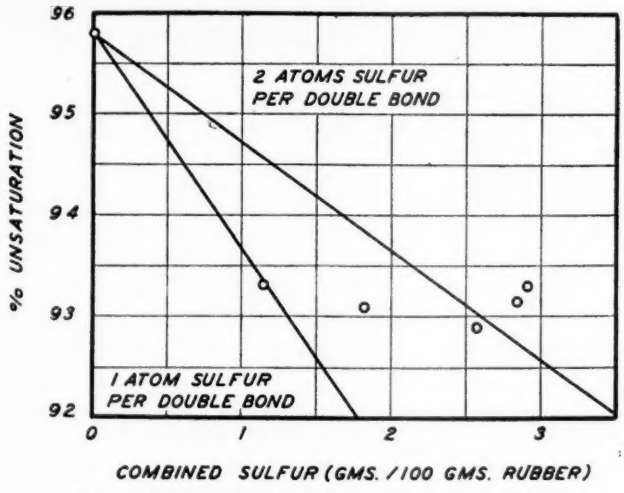

FIG. 6.—Sulfur combination *vs.* unsaturation of total rubber.

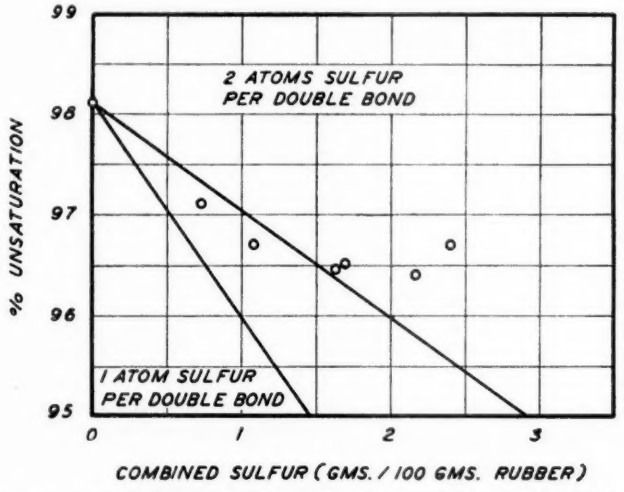

FIG. 7.—Sulfur combination *vs.* unsaturation of low molecular-weight sol rubber.

on the coefficient of vulcanization, which depends on the amount of combined sulfur, and furthermore did not realize when carrying out their experiments that they had inadvertently fractionated the rubber they partially dissolved in benzene. Therefore, they really must be considered to have been the first who studied the properties of fractionated rubber.

Thus, it can be argued that as vulcanization continues, it is possible to introduce a far greater amount of sulfur bridges into sol rubber—before an appreciable difficulty in chain slippage occurs—than into gel rubber. Also, the tensile strength increases as we are still lengthening the comparatively short chains without hindering their respective mobility too much. Likewise we may expect that the effect of lengthening the chains by sulfur bridges will be more pronounced for the short chains of sol rubber than for the already long chains of gel rubber.

It seems plausible that for gel rubber we obtain what is called optimum cure—as judged by the tensile product—in a shorter time and with fewer sulfur bridges than are necessary to obtain the same effect for sol rubber. These considerations also seem to be brought out by the greater drop in the slope of the elongation curve with time of cure for gel rubber than for sol rubber. It would also indicate that the state of vulcanization of gel rubber is different from that of sol rubber if both are considered at their optimum cure. It furthermore indicates that the actual amount of sulfur bridges in itself, as introduced between rubber molecules in general, is really of secondary importance only, in regard to their physical properties, and that the kind of sulfur bridge formed between the chains would not have too great a bearing on the physical properties.

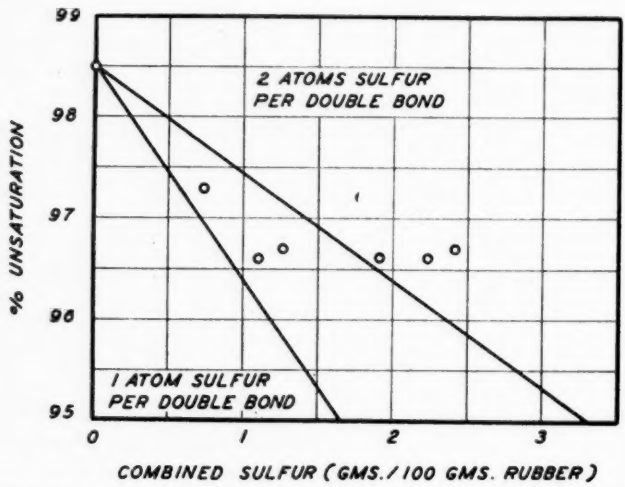

FIG. 8.—Sulfur combination *vs.* unsaturation of high molecular-weight sol rubber.

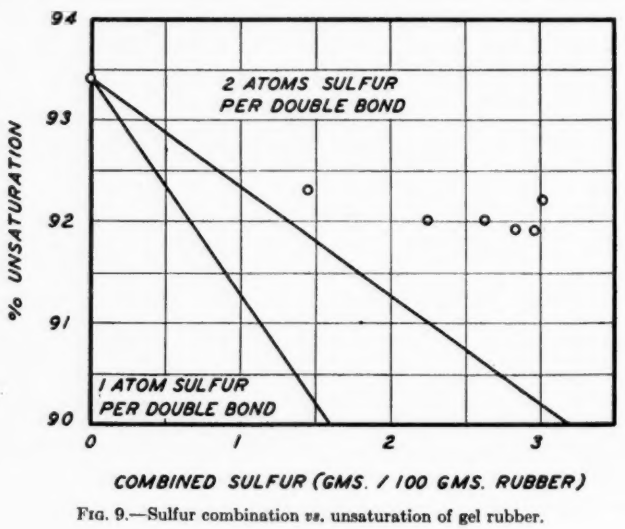

FIG. 9.—Sulfur combination *vs.* unsaturation of gel rubber.

However, the effect of optimum vulcanization is obtained at any time at which we have introduced the correct amount of sulfur bridges for the particular kind of rubber molecules we are dealing with. This amount is governed by the structure and length of the molecules, their entanglement and cohesive forces acting between them.

Carothers[13] states that "the cohesive forces which resist the separation of molecules from one another (as measured, for example, by the heat of vaporization) increase continuously with increasing molecular weight in a given series, and in high polymers they reach values greatly in excess of the energy required to rupture a primary valence linkage in a chain". Bolland[14] calculated that because of resonance effects the least dissociation energy necessary to rupture such a bond would amount to 43,000 cal. per mole. Carothers' statement implies that the cohesive forces in gel rubber would be greater than in sol rubber.

If sulfur bridges are introduced, fewer of them would be necessary to produce "optimum cure" in gel rubber than in sol rubber, because an increase in sulfur bridging tends to shorten the former's elongation; whereas in sol rubber this latter point is reached only at a later stage, and a chain lengthening effect without the occurrence of too great interference between the chains is predominant in the beginning. There is no justification for the assumption that a different kind of sulfur bond is produced during vulcanization of sol rubber and of gel rubber.

Therefore, it is possible that several phenomena occur to produce the final effect of acceleration of vulcanization caused by nitrogen-containing compounds in natural rubber. It is known that the solubility of sulfur in rubber is greatly influenced by temperature. Migration of sulfur in rubber occurs by diffusion. Venable and Green[15] found this migration to be more and more retarded by progressive vulcanization. If the initial rate of vulcanization is high (and it could be speeded by the presence of nitrogen-containing compounds in the rubber), migration of sulfur is quickly impeded. Free sulfur, located within the network formed around it by vulcanization, may not be reached by the analytical procedure, and would, therefore, wrongly be accounted for as combined sulfur. Such a condition, of course, would be more pronounced in gel rubber than in sol rubber because of the original structure of the former.

SUMMARY

Hevea prime ribbed smoked sheets were subjected to diffusion fractionation. The rubber recovered from the separate fractions was compounded and vulcanized. The physical and chemical properties of the vulcanizates showed pronounced differences. A tentative explanation for these results is offered on the basis of the molecular and colloidal structure of the rubber hydrocarbon.

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THE MECHANISM OF REINFORCEMENT. II*

GEORGE GOLDFINGER

GODFREY L. CABOT, INC., BOSTON, MASACHUSETTS

In an earlier paper[1] it was shown that, when a dilute (1 per cent) solution of GR-S in xylene is thoroughly mixed with carbon black and the carbon black is then precipitated by centrifuging, the GR-S recovered from the "treated" solution has a higher modulus than GR-S recovered from an equivalent solution which is not treated with carbon black. This phenomenon suggests that the reinforcing effect of carbon black might be due partially to the specific adsorption of certain fractions of the gum stock on the carbon black surface, leaving a tougher fraction in between the carbon black particles.

To gain more information on the subject, a number of experiments were carried out with varying proportions of carbon black. In the first set of experiments 50, 100, 200, and 400 grams of Sterling-R furnace black (surface area 25 sq. meters per gram) were added to 100 grams of GR-S dissolved in 10,000 grams of xylene. The mixture was then agitated and finally centrifuged to separate the carbon black. The clear supernatant solution was precipitated in ten times its volume of methanol, and the precipitated GR-S was vacuum-dried. The GR-S thus reclaimed was compounded with a standard master batch (reclaimed GR-S, 8.0; GR-S, 2.0; sulfur, 0.2; Santocure, 0.1; zinc oxide, 0.5; Bardol, 0.6; pine tar, 0.3 parts). One-half of this compound was then loaded with 5 parts carbon black per 100 parts GR-S and the other half with 50 parts carbon black per 100 parts by weight GR-S. For a control, a sample of the 1 per cent GR-S solution was carried through the entire treatment without addition of carbon black to the solution. The experimental procedure is described in detail in Part I of this study[1].

A second group of experiments were carried out in which the carbon black was first dispersed in dry GR-S on a roll mill, and a xylene cement was then prepared from this stock; 20 grams of GR-S was milled for 45 minutes at 5°C between tight rolls on a 2″ × 6″ mill; 10 grams of Sterling-R carbon black was then added within the next 15 minutes. These two samples were then each dissolved in 2000 grams of xylene and centrifuged, precipitated, dried, and compounded as described above. Finally, an attempt was made to identify the GR-S fraction which was carried from the suspension by the carbon black on centrifuging. The carbon black-rubber precipitate obtained on centrifuging the 400 grams of Sterling-R, 100 grams of GR-S cement was redissolved in 10,000 grams of xylene. GR-S was then recovered from the supernatant cement obtained on centrifuging, and compounded as described above. The entire procedure is outlined schematically in Figure 1.

The samples were cured 60 and 90 minutes, respectively, and stress-strain values obtained with a Scott inclined-plane tester. First and tenth elongation-contraction cycles were recorded. The data for the 60-minute cures are given

* Reprinted from the *Journal of Polymer Research*, Vol. 1, No. 1, pages 58–62, January 1946. The present address of the author is Chemistry Department, University of Buffalo, Buffalo, N. Y.

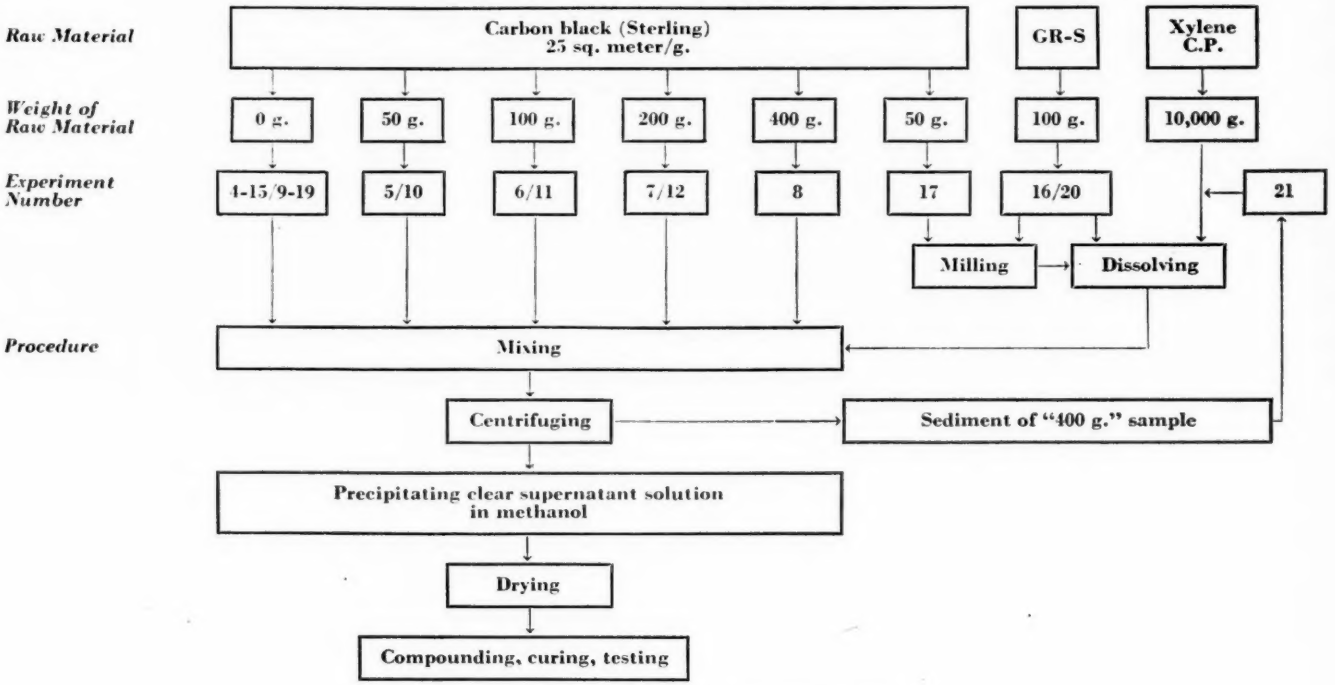

FIG. 1.—Schematic representation of the experimental procedure.

in Figure 2. The results for 90-minute cures are essentially the same. Comparison of the data obtained in the first group of experiments in which varying proportions of carbon black were added to the rubber cement and mixed shows that increasing proportions of carbon black in the cement induced an increase in stiffening of the stock prepared from the recovered GR-S when compounded with 5 parts of carbon black. If, however, the recovered GR-S is compounded with 50 parts of carbon black, then increasing proportions of black used in the treatment of the cement proportionally reduces the stiffness of the compounded stock. In the series of experiments in which the carbon black was milled into GR-S and the milled stock was dissolved and treated, the stiffening effect of the treatment is considerably larger than in the case in which the carbon black was added to the solution (Figure 3). The reason might well be that, when the

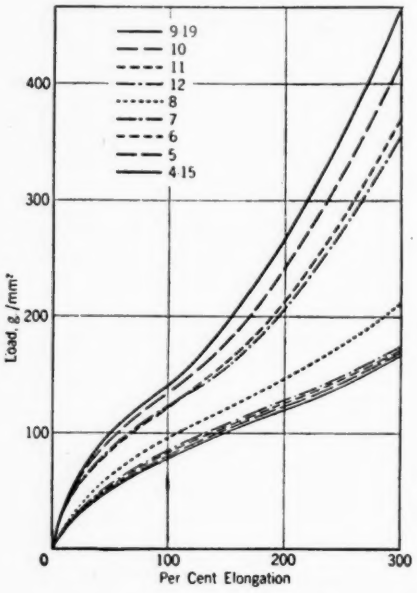

FIG. 2.—Load-elongation curves of 60-minute cured samples of GR-S recovered from solution after treatment. The numbers are the sample numbers as given in Table I.

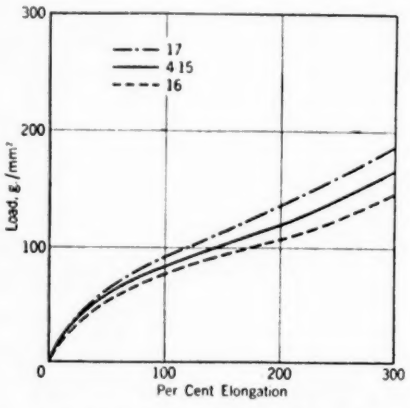

FIG. 3.—Load-elongation curve of 60-minute cured samples of GR-S. The increase of the stiffening effect by milling the carbon black in the GR-S before dissolving is shown. Curve 17 is obtained from a sample on which 50 parts of carbon black was milled before dissolving the sample; curve 4–15 is the average value of the control run as used in Figure 2; 16 is the control run in which GR-S was milled but no pigment added before dissolving.

black is added to the solution, only a small fraction of the surface participates in the process which induces the changes in rubber properties of the recovered rubber, whereas, if milled in, essentially the entire surface participates. Electron-microscope pictures of the sediment obtained on centrifuging the mixture carbon black-GR-S-cement support this view. The pictures show that an appreciable fraction of the carbon black was not wetted by the rubber[2].

The reversal of effect of treatment of the solution, depending on whether compounding of recovered GR-S was carried out with 5 or 50 parts of carbon black, is shown in Figure 4, in which the ratio of modulus of the 50-part loaded stock *vs.* the 5-part loaded stock is given.

In an attempt to gain information on the nature of the material supposedly adsorbed on the carbon black, the sediment obtained on centrifuging a cement

(400 g. black, 100 g. rubber) was leached with xylene and carried through the centrifuging, precipitating cycle. The rubber recovered from this treatment was compounded and cured. However, even after 90 minutes, the stock was so decidedly undercured that the sample could not be removed from the mould.

In an earlier publication on this subject[1] it was suggested that the carbon black preferentially adsorbs a weaker fraction of the rubber and hence leaves a stiffer fraction to compose the rubber matrix whose properties are measured. With the additional experimental evidence now available, this picture is further supported and can be extended. The rubber can be visualized as a mixture of a series of components which are adsorbed with increasing ease by the carbon black, but which contribute decreasingly to the stiffness of the rubber matrix—for example, molecular fractions with increasing concentration of styrene in the case of GR-S. When the rubber cement is treated with carbon black, a portion of this "weaker" component is adsorbed and removed. Hence, when the

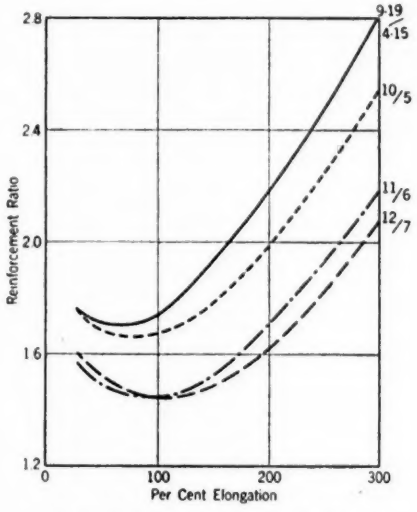

FIG. 4.—Ratio of the modulus of 50 parts of carbon black vs. 5 parts of carbon black loaded stock. The effect of treatment on the reinforcement ratio is shown. The numbers are the sample numbers as given in Table I.

compounding of the recovered rubber is carried out as pure-gum stock (5 parts of carbon black) it is found that, with increasing proportions of carbon black in the cement, a corresponding stiffening of the stock occurs. When, however, the recovered rubber is compounded with carbon black (50 parts), then the removal of the "weaker" fraction weakens the stock because less of this material is available to form a tight adsorbed layer around the carbon black and thus the effective volume of the black is not increased so much as in the compound from untreated rubber. If the effect is due to adsorption of styrene-rich fractions, then it can be assumed that the presence of those fractions in pure-gum compounds weakens the stock by not participating in the vulcanized network. In a carbon black compounded stock, however, the styrene-rich fractions would be removed from the matrix in any event. Their presence could not manifest

itself by "diluting" the gum part of the compound, but by increasing the effective volume of the carbon black and, hence, stiffening the stock. This interpretation is supported by the fact that rubber recovered from the precipitated carbon black could not be cured.

Measurements were also carried out to determine the changes in viscosity as a result of the carbon black treatment of GR-S cements. No further information has been gained beyond that already published in the previous paper. The viscosity of the sample recovered from the sedimented carbon black was found to be considerably lower than that of the original sample.

TABLE I

LIST OF EXPERIMENTS AND THEIR IDENTIFICATION NUMBERS

Sample No., compounded with carbon black		Parts carbon black (per 100 parts GR-S) used in treatment of solution	Remarks
5 parts	50 parts		
4	15	None	
9	19	None	
5	10	50	
6	11	100	
7	12	200	
16	20	None	GR-S milled 60 minutes
17	..	50	GR-S milled 45 minutes, carbon black added in 15 minutes

An attempt to determine the actual amount of rubber adsorbed on carbon black failed. Such a determination cannot be carried out by weighing back the dried sediment because considerable quantities of rubber are occluded in the spaces between the individual carbon black particles. Therefore an attempt was made to determine this fraction by measurement of change in concentration of the clear supernatant cement. Experiments, carried out with all possible care and reproducible within 0.3 per cent, did not, however, show any difference in concentration of the supernatant rubber solution where the carbon black concentration was varied from 0 to 300 per cent of the rubber. This undoubtedly is due to the fact that the adsorbed polymer is as highly swollen as the dissolved polymer within at least ± 0.3 per cent, and hence no change in the concentration of the rubber cement is detectable.

ACKNOWLEDGMENT

The author is very much indebted to Godfrey L. Cabot, Inc., for permission to publish the present data. He further wishes to acknowledge the kind assistance of Charles B. Wendell and Ann W. Sullivan in designing the apparatus and collecting data, and the valuable help of Cecil Hall, Massachusetts Institute of Technology, for a number of electron micrographs of the various sediments.

SUMMARY

Further experimental evidence is given which indicates that, when a dilute solution of GR-S is mixed with carbon black, certain fractions of the rubber are preferentially adsorbed by the black. After removal of the carbon black and the adsorbed fractions by centrifuging, the "treated" GR-S is obtained by precipitation from the solution. Samples compounded as GR-S gum stock

show increasing modulus with increasing amounts of carbon black used for adsorption treatment. However, when the GR-S thus treated is compounded with carbon black, then the effect is reversed. The more black used in the treatment and the higher the modulus of the gum stock, the lower the modulus of loaded stock.

REFERENCES

[1] RUBBER CHEM. TECH., 18, No. 2, 286 (1945).
[2] Since electron micrographs are notoriously poor in print, the author prefers not to present here the very excellent pictures taken by Cecil Hall.

SPECIFIC HEATS OF HEVEA, GR-S, AND GR-I STOCKS *

W. H. HAMILL, B. A. MROWCA, AND R. L. ANTHONY

UNIVERSITY OF NOTRE DAME, INDIANA

Accurate knowledge of the specific heats of various natural and synthetic rubber stocks is necessary for the thermodynamic study of rubberlike materials. For example, the correlation between the entropy component of the stress-strain curve and the reversible heat developed when rubber is stretched rapidly[1] requires knowledge of the specific heat of the rubber as a function of elongation and of temperature. Knowledge of the specific heat is also needed in correlating calculated energy losses with rise in temperature in flexometer experiments.

For the thermodynamic studies mentioned above, c_L, the specific heat at constant length, is needed. The dependence of c_L on the elongation was measured by Ornstein, Wouda, and Eymers[2] and by Boissonas[3] with conflicting results. Ornstein, Wouda and Eymers obtained a strong dependence of c_L on elongation. Boissonas found constancy of c_L for a cured stock, while for crude Hevea c_L increased very slightly with elongation. The present paper points out that for regions without crystallization the observed dependence of the stress on the temperature necessarily leads to a constancy of c_L up to the fourth decimal. Thus, for all practical purposes, c_L may be considered identical with c_p.

Many workers have measured the specific heats of various types of rubber stocks. Results of earlier work are listed in standard treatises on the subject[4], but the great majority of the published results are of little value for purposes of thermodynamic calculations. In some cases the rubber stock employed was not sufficiently defined as to composition. In others the values are definitely unreliable because of rather dubious experimental techniques. Some recent values of considerable interest are those of Boissonas[3], those of Roth, Wirths, and Berendt[5] and those of Fouts[6]. These values will be discussed later in the paper.

Recognizing the need for accurate thermodynamic data on rubber, under well defined conditions, the National Bureau of Standards[7] has for some years been carrying out a program of supplying such information for various unvulcanized rubbers. As a result of their work accurate values of specific heat at constant pressure are now available for purified natural rubber, Hycar OR-15, and GR-S over a continuous range of temperatures from absolute zero to well above room temperature.

Most investigations of the equation of state of rubber, studies of stress-temperature relations, and studies of heat build-up employ vulcanized stocks containing all the usual ingredients, such as fillers, reinforcing agents, accelerators, etc. Specific heat values for such compounds are required for complete investigations of this nature. It is of interest to see whether or not specific

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 38, No. 1, pages 108–110, January 1946.

heats can be calculated, with good accuracy (better than 1 per cent), for stocks of this type by employing the values supplied by the Bureau of Standards for the crude rubbers and adding the fractional specific heats for the various ingredients.

Accordingly, an adiabatic type calorimeter was constructed, and specific heat measurements were made in the region of room temperature on Hevea and GR-S gum and tread stocks. Data were also taken on raw GR-I (Butyl B—1.45) and on a GR-I gum stock. The values obtained are in excellent agreement with the values calculated from the fractional specific heats. The calorimeter employed in this work is described. This calorimeter yields results having a precision much better than those obtained by simple mixture methods, and yet it can be operated rapidly enough to measure the specific heat of a new polymer in a few hours.

DESCRIPTION OF CALORIMETER

The calorimeter, *C*, Figure 1, is of the adiabatic type. It is surrounded by a jacket, *J*, whose temperature is held closely equal to that of the calorimeter; thus, as far as practical, heat flow to or from the calorimeter is eliminated. The jacket is constructed in two parts; the side walls and base constitute one part and a removable watertight top, the other. Both parts of the jacket are made entirely of copper sheet and are of double wall construction. For operation at only a few degrees above room temperature it was found necessary to eliminate the constant heat input into the jacket resulting from the stirring action of pump *P*. This was accomplished by means of the condenser *E* placed between the pump and jacket, cooling being provided by ordinary tap water. A tube soldered to the bottom of the calorimeter provides a close fitting container for the Beckmann thermometer B_1. About 1 cc. of ethylene glycol placed in the tube gives effective heat contact between the calorimeter and Beckmann thermometer. A copper-constantan thermocouple, *T*, with junctions soldered, respectively, to the inside wall of the jacket and to the outside of the calorimeter wall, provides a means of maintaining the temperature of the inside wall of the jacket closely equal to the temperature of the outside surface of the calorimeter. This thermocouple actuates a galvanometer photocell relay circuit to maintain the desired adiabatic condition (Figure 2). While mercury thermostat *D* is not necessary to the operation of the calorimeter, it is very convenient. By connecting jacket heater, H_2 to the thermostatic control circuit a couple of hours in advance of a run, the jacket and the calorimeter in the interior space are automatically brought to the predetermined starting temperature.

CALIBRATION AND OPERATION

The calibration of the calorimeter was carried out by using known amounts of pure aluminum and copper rods. The rods were placed loosely in the space to be occupied by the rubber. The calorimeter and jacket were then brought up to the starting temperature of about 26° C by the thermostatic control circuit; then the system was connected to the photocell control circuit. After thermometer B_1 had reached a steady value and no change in temperature could be detected over a period of 15 to 20 minutes, switch S_4 was thrown, simultaneously connecting the calorimeter heater, H_1, to the storage batteries and also starting the split-second timer, *M*. The heating time was usually about 20 minutes, and the current (of the order of 0.1 ampere) was measured period-

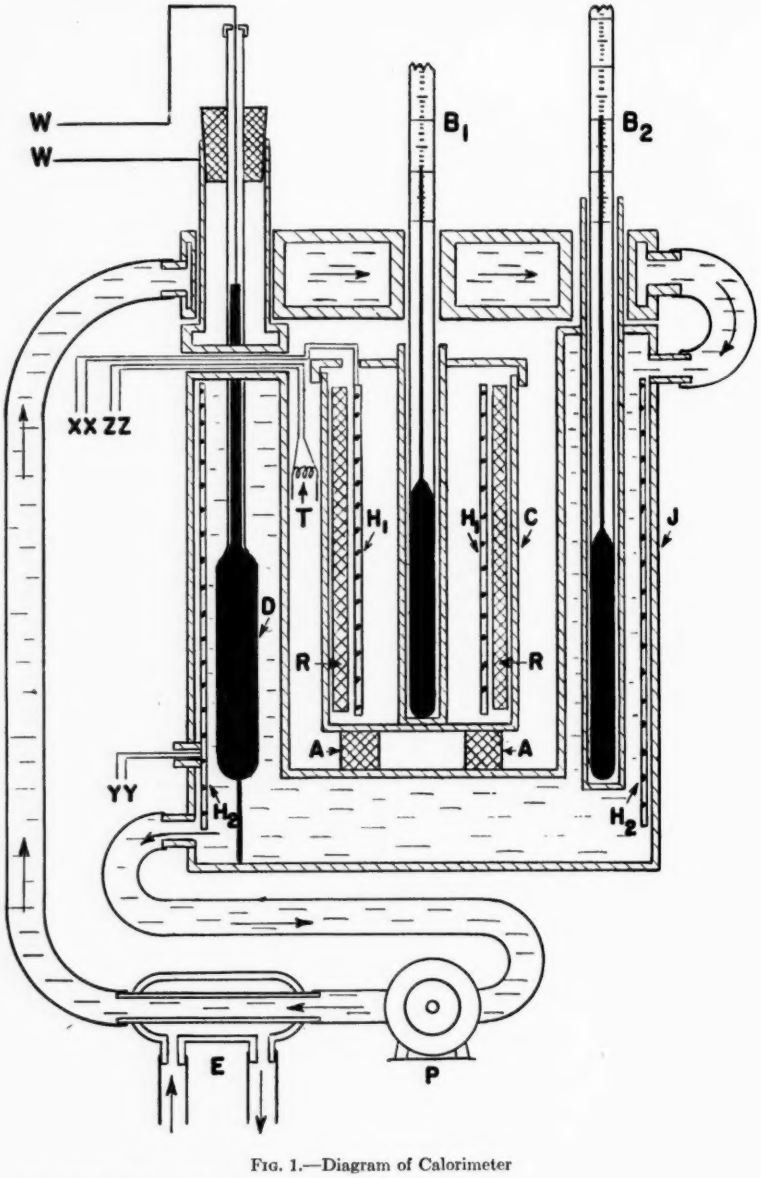

FIG. 1.—Diagram of Calorimeter

A. Three small Bakelite insulating supports, about ¾ inch high
*B*1. Calorimeter Beckmann thermometer
*B*2. Jacket Beckmann thermometer
C. Calorimeter
D. Mercury thermostat
E. Condenser
*H*1. Calorimeter heater, 49.3 ohms
*H*2. Jacket heater
J. Jacket
P. Circulating pump
R. Rubber test sheets
T. Copper-constantan thermocouple
WW. Leads to mercury thermostat *D*
XX. Leads to calorimeter heater *H*1
YY. Leads to jacket heater *H*2
ZZ. Leads to thermocouple *T*

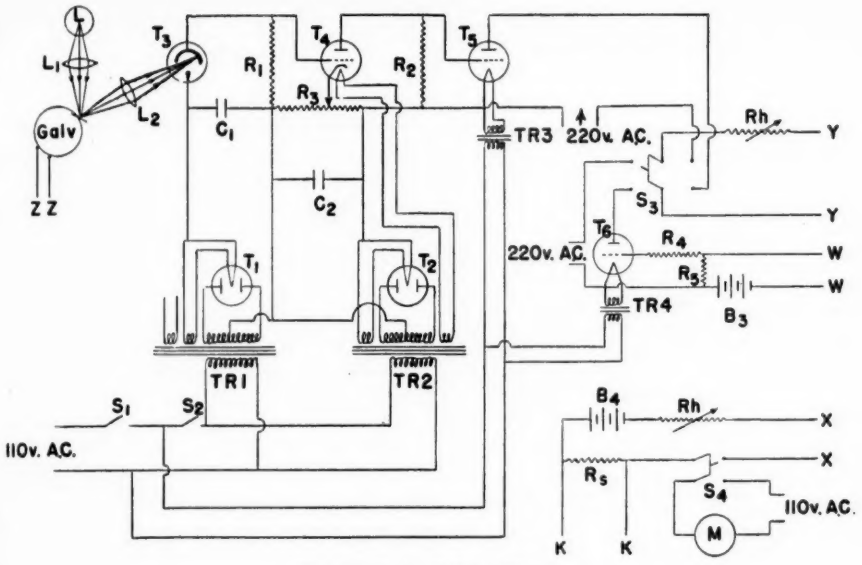

FIG. 2.—Photocell Relay Circuit

B_3. 45-volt B-battery
B_4. 12-volt storage battery
C_1. 8-microfarad condenser
C_2. 16-microfarad condenser
M. Split-second timer
R_1, R_2. 7-megohm resistance
R_3. 43,700-ohm potentiometer
R_4, R_5. 50,000-ohm resistance
Rh. Low-resistance rheostat, 100 ohms
R_s. Leeds & Northrup standard 1-ohm resistance
T_1, T_2. 5W4
T_3. 919
T_4 6K5G
T_5, T_6. FG 27A
$TR1$, $TR2$. 750 volts, c. t., 6.3 volts, 5-volt transformers
$TR3$, $TR4$. 5-volt, 5-ampere transformers
Galv. Leeds & Northrup type HS galvanometer of sensitivity 0.08 microvolt/mm.
L. 6–8 volt, 50-watt automobile-type lamp
L_1. Lens of short focal length and large diameter, placed close to L
L_2. Lens of long focal length
S_1, S_2. s.p.s.t. switches
S_3, S_4. d.p.d.t. switches
KK. Leads to potentiometer
WW. Thermostat leads
XX. Calorimeter heater leads
YY. Jacket heater leads
ZZ. Thermocouple leads

ically during the run by means of a Leeds & Northrup type K-2 potentiometer. At the end of the heating period the temperature of the calorimeter was again observed until a constant value was reached and maintained over a 15–20 minute period. A total drift of less than 0.001° C over the period preceding the run and also at the end of the run was the criterion employed for constant end temperatures. The temperature rise employed, both for the calibration and also in the later runs on rubber, was usually about 1.5° C. The heating current to the calorimeter and the heating time were adjusted always to employ the same range on the Beckmann thermometer as that used in the calibration. It should be noted that the thermocouple photocell control circuit automatically maintains the temperature of the inner wall of the jacket closely equal to that of the outside surface of the calorimeter, not only at the start and end of the run, but also during the heating period. This condition is achieved in practice at the start of the run by sliding the photocell back and forth across the light beam from the galvanometer with a rack and pinion drive, until the constant temperature conditions described above are obtained.

The average of ten runs, employing copper rod for three of the runs and aluminum for the other seven, gave the following value for the heat capacity

of the calorimeter:

$$H_{cal} = 36.26 \pm 0.12 \text{ cal. per } ^\circ \text{C at } 26\text{–}27^\circ \text{C}$$

Since the materials used in the calibration were good conductors of heat, and since it was planned to use the calorimeter to measure specific heats of rubberlike materials which are poor heat conductors, it was decided to check the specific heat of some nonconducting material. Sodium chloride was selected, and the average value for three runs was:

$$C_p = 0.206 \pm 0.001 \text{ cal. per gram per } ^\circ \text{C at } 26\text{–}27^\circ \text{C}$$

The value to be expected at 26° C, according to Kelley[8] is 0.206 cal. per gram per ° C. The procedure employed in the rubber runs was identical with that described above for the calibration; the heat capacity of the rubber in each case was approximately equal to or greater than that of the calorimeter itself.

Although the calibration and later runs on the various rubber stocks were carried out in the temperature region 26–27° C, the calorimeter can be adjusted to operate in the same fashion at other temperatures. Use of a liquid such as ethylene glycol, with perhaps better heat insulation, would permit operation at temperatures less than 0° and greater than 100° C.

STOCKS INVESTIGATED

Compositions of the stocks studied are given in Table I. The samples were in the form of standard 6 × 6 inch test sheets. Two or three such sheets were inserted in the calorimeter. No spiral provisions for better thermal contact seemed to be required.

TABLE I

COMPOSITION OF RUBBER STOCKS IN PARTS BY WEIGHT

Stock	A	B	C	D	E	F	c_p, cal. per g. per ° C at 26–27° C
Smoked sheet	100.00	100.0	..	..	..	..	0.452
GR-S	..	..	100.0	100.0	..	..	0.454
GR-I (Butyl B-1.45)	..	..	..	..	100.0	100.0	..
Standard Micronex	..	52.0	..	50.0	..	..	0.18
Zinc oxide	3.0	3.0	5.0	5.0	..	5.0	0.118
Stearic acid	4.0	4.0	..	..	..	3.0	0.40
Pine tar	2.0	2.0	..	..	..	..	0.50
Sulfur	2.7	2.7	2.0	2.0	..	1.5	0.16
Betanox	1.5	1.5	..	..	..	..	0.50
Captax	0.9	0.9	1.5	1.5	..	..	0.50
Tuads	..	..	..	..	..	1.0	0.50
Bardol-B	..	..	5.0	5.0	..	..	0.50
Total conditions of vulcanization	114.1	166.1	113.5	163.5	100.0	110.5	..
Minutes	40	60	60	60	..	70	..
Temp (°F)	274	274	298	298	..	307	..
Density at 26–27° C (g. per cc.)	0.964	1.122	0.987	1.165	0.910	0.961	..

The results are given in Table II. The measured value of c_p is given both in calories per gram per ° C and in calories per cc. per ° C. Each tabulated measured value is an average of at least three runs. The reproducibility in each case was 0.001 calorie per gram per ° C or better. All measurements are

TABLE II

SPECIFIC HEATS OF SODIUM CHLORIDE AND RUBBER SAMPLES

Sample	Type of stock	Calcd. c_p, cal. per g. per ° C	Measured c_p	
			cal. per g. per ° C	cal. per cc. per ° C
NaCl	....	..	0.206	..
A	Hevea gum	0.436	0.437	0.421
B	Hevea tread	0.356	0.357	0.401
C	GR-S gum	0.435	0.437	0.431
D	GR-S tread	0.357	0.358	0.417
E	Raw GR-I	..	0.464	0.422
F	GR-I gum	0.443	0.443	0.426

at 26–27° C, and all correspond to a temperature rise of about 1.5° C. For comparison the calculated value of c_p is also included. In the case of raw GR-I (Butyl B-1.45) no comparative values were available. The specific heat of sample F was calculated from the measured value of sample E.

For calculating c_p, the specific heat values listed in Table I were employed. The value for Hevea rubber was given by Bekkedahl and Matheson[9], and for GR-S, by Rands, Ferguson, and Prather[10]. No special attempt was made to secure accurate values of specific heats for the various ingredients other than for the rubber itself and for carbon black. The figure used for carbon black is discussed later in this paper. The values for zinc oxide, stearic acid, and sulfur are taken from the literature[11]. The figure of 0.5 for pine tar, Captax, Betanox, and Bardol B is estimated. However, these values do not need to be known accurately, since the majority of these ingredients usually enter into the compound as very small percentages of the total or have small specific heats themselves. To illustrate the procedure, the calculation of c_p for sample A is shown:

$$c_p = [(100 \times 0.452) + (3 \times 0.118) + (4 \times 0.40) + (2 \times 0.5) + (2.7 \times 0.16) + (1.5 \times 0.5) + 0.9 \times 0.5)]/114.1$$
$$= 0.436 \text{ cal. per gram per } ^\circ \text{C.}$$

Table II shows that in all cases the agreement between the calculated value of c_p and the measured value is considerably better than 1 per cent. When expressed in terms of calories per cc. per ° C rather than of calories per gram per ° C, the large differences in the values of the specific heats vanish, and the values for the stocks measured lie between 0.401 and 0.431 calorie per cc. per ° C. The value of specific heat in calories per cc. per ° C is important in the thermodynamic study of rubber.

DISCUSSION

Boissonas[3] in 1939 reported specific heat values at 20° C for two types of samples as functions of elongation over the range 0–200 per cent extension. In sharp contrast to earlier work by Ornstein, Wouda, and Eymers[2], Boissonas found no variation in the specific heat when measured as a function of extension at 20° C for his first sample, and only a slight variation, if any, for his second sample. Accordingly his results have been averaged, and only the average value for each sample is given here. For his first sample, consisting of 89 parts of smoked sheet, 1.8 parts of sulfur, 0.9 part of accelerator, and 8.3 parts of zinc oxide and carbon black, vulcanized 30 minutes at 3 atmospheres, Boissonas reports a set of values whose average is 0.378 calorie per gram per ° C. For his second sample, a pure crepe; the average of the values reported by

Boissonas is 0.41 calorie per gram per ° C. The second value is considerably lower than the value of c_p for rubber at 20° C as given by Bekkedhal and Matheson[9]—namely, 0.443 calorie per gram per ° C. Using the value of 0.443 and calculating the specific heat for Boissonas' first sample, we obtain 0.404 calorie per gram per ° C. It appears, then, that the values reported by Boissonas are somewhat low.

Roth, Wirths, and Berendt[5] reported a value of $c_p = 0.472 \pm 0.004$ calorie per gram per ° C for crude untreated Buna-S. This value is an average for the temperature range 20–50° C. According to the results of Rands, Ferguson, and Prather[10] the average value of the specific heat of GR-S over the same temperature range is 0.461 calorie per gram per ° C. Since the equivalence of the two stocks is somewhat questionable, it is not certain whether the average value reported by Roth, Wirths, and Berendt is too high or not.

Fouts[6], using a simple mixture method, obtained the following specific heat values:

Stock	c_p, cal. per g. per ° C	Temp. range (° C)
Crude GR-S	0.458	99–27
Pure gum GR-S	0.464	99–27
GR-S	0.383	99–34
Natural rubber tread	0.378	99–27

Rands, Ferguson, and Prather[10] find that over the temperature range $-50°$ to $+60°$ C the specific heat for GR-S is given precisely by:

$$c_p = 0.4346 + 7.029 \times 10^{-4}\, t + 1.156 \times 10^{-6}\, t^2$$

Assuming that this expression holds reasonably well up to 100° C, integrating from 20° to 100° C, and dividing by the temperature difference to obtain the average value of c_p over this range yields $c_p = 0.482$ calorie per gram per ° C. The calculated average over an even lower temperature range, 20° to 60° C, is 0.469 calorie per gram per ° C. It thus appears that the value 0.458 calorie obtained by Fouts for crude GR-S is too low. Fouts did not know the composition of this particular sample, but he described it as being very sticky and it may, therefore, have differed appreciably from the usual crude GR-S stock. It is difficult to see why the value for a pure gum GR-S should be greater than that for the crude GR-S, since most of the ingredients entering into the pure gum stock (with the exception of relatively large amounts of organic compounds) would lead to a smaller specific heat. Hence one would expect c_p for the pure gum GR-S to be less than that for the crude stock. Since the compositions of the two tread stocks measured by Fouts are not known, it is not possible to calculate these specific heats.

In the case of tread stocks and other similar stocks containing carbon black, it appears that the specific heat of the carbon black used is close to that of graphite. The x-ray study of carbon blacks by Biscoe and Warren[12] shows that carbon black particles are not small graphite particles. Rather each carbon black particle is found to be an agglomerate or mixture of disordered parallel layer groups. The structure of these parallel layer groups is, however, very similar to that of graphite. In the case of tread stocks, where the amount of carbon black may be of the order of 50 parts by weight of carbon black to 100 parts of rubber, the total specific heat, *i.e.*, per gram of stock, is quite sensitive to the value of the specific heat of carbon black. As a matter of fact, the value of $c_p = 0.18$ for carbon black was determined in this work by calculating the

figure needed to make the calculated c_p for stock B agree with the measured c_p for the same stock. This value is identical with the specific heat of graphite. (Although the c_p figure for carbon black needed for complete agreement between the measured and calculated values for stock B is 0.183, the estimated precision in this determination warrants the use of only two significant figures. Using 0.18, then, instead of 0.183, the calculated value for stock B becomes 0.356 rather than 0.357.)

The value 0.18 refers to standard Micronex in the rubber matrix. A separate study would be necessary to recognize a possible difference between the specific heat of the carbon black alone and when compounded in rubber. Such a difference may arise from the interaction between carbon black and rubber.

In connection with the results of Ornstein, Wouda, and Eymers and those of Boissonas, it is of interest to point out that c_L, the specific heat at constant length (and at the same temperature), should not vary appreciably with elongation over the range 0 to 200 per cent extension and 0° to 70° C for most rubber-like materials. This is true, provided no phase changes occur in this region. In the case of many rubbers, both natural and synthetic, both the range of extensions and the range of temperatures may be increased without altering the argument. The essential requirements are that in the region under consideration phase changes must not occur, and the stress at constant length must be approximately a linear function of temperature. This condition has been shown to exist for the natural and synthetic rubbers studied[13]. If the stress at constant length is accurately linear in the temperature, then it may be shown on purely thermodynamic grounds[14] that c_L cannot vary with change in length. Suppose, however, that the stress-temperature curves at constant length are not straight lines and, hence, that the slopes of these lines are functions of the absolute temperature. Then:

$$\left(\frac{\partial Z}{\partial T}\right)_L = r + sT \tag{1}$$

where r and s are constants. Let us further suppose that there is a 5 per cent uncertainty in the slope of the experimental stress-temperature curves or a deviation from linearity of 5 per cent in these curves—*i.e.*, that the term sT in Equation 1 amounts to about 5 per cent of term r. (Actually a deviation from linearity as great as this would be easy to detect, and was not observed in any of the work referred to above in the regions under consideration, provided crystallization did not set in.) By how much, then, will c_L vary with length? Let us assume a linear variation of c_L with L of the form:

$$c_L = a + bL \tag{2}$$

where a and b are constants, L is the relative length, defined as the ratio of the extended length of the sample to the unloaded length measured at room temperature. In this connection it should be noted that stress Z is really the total force on a sample whose unloaded cross section at room temperature is 1 sq. cm. Also, the relative length, L, may be interpreted as the actual extended length of a sample whose unloaded length at room temperature was 1 cm. Hence the fundamental amount of rubber considered in a thermodynamic discussion of this nature is 1 cc. and not 1 gram. As a result, c_L is to be interpreted as the specific heat at constant length of the rubber, measured in calories per cc. per ° C and not in calories per gram per ° C.

If an equation of state exists, it may be shown[14] that:

$$\left(\frac{\partial c_L}{\partial L}\right)_T = -T\left(\frac{\partial^2 Z}{\partial T^2}\right)_L \tag{3}$$

Combining Equations 1, 2, and 3:

$$b = -sT \tag{4}$$

An average value for the rate of increase of stress with temperature at constant elongation (in the region 200 to 300 per cent) is:

$$r = 60\ grf \text{ per } ^\circ \text{C}$$

Taking sT as 5% of this value and T as 300° K:

$$b = -3\ grf \text{ per } ^\circ \text{C} = -2.94 \times 10^{-4} \text{ joule per } ^\circ \text{C per cm.}$$

or

$$b = -0.703 \times 10^{-4} \text{ cal. per } ^\circ \text{C per cm.}$$

Hence at 0 per cent, $c_{L=1\text{ cm.}} = a - 0.703 \times 10^{-4}$ cal. per ° C; at 200 per cent, $c_{L=3\text{ cm.}} = a - 3 \times 0.703 \times 10^{-4}$ calorie per ° C. So the total change in c_L to be expected over the range 0 to 200 per cent is:

$$\Delta c_L = -0.00014 \text{ cal. per } ^\circ \text{C (per cc. of rubber)}$$

This is a negligible contribution to the specific heats of most rubbers $\cong 0.400$ calorie per cc. per ° C at room temperature. Hence for practically all rubbers investigated to date for which a straight-line equation of state has been shown to exist, the variation of c_L with L appears to be negligibly small. Hence c_L and c_p are experimentally indistinguishable.

SUMMARY

1. A calorimeter, suitable for determining the specific heats of various rubber compounds (with a precision of 1 per cent or better), is described. Although the results reported are for room temperature (actually 26–27° C), the calorimeter could be operated with minor changes at other temperatures.

2. Employing values of the specific heat at room temperature as given by the National Bureau of Standards[15] for various raw rubbers, it is shown by direct measurement on various gum and loaded stocks that the specific heats of these materials can be calculated from a knowledge of the specific heats of the ingredients.

3. A 5 per cent deviation from linearity in the stress-temperature curves at constant length can cause a total variation in c_L of only about 0.00014 calorie per cc. per 1° C over an elongation range of 0 to 200 per cent. This result holds, provided an equation of state exists and provided the region of temperature and elongation considered is one in which phase changes do not occur. Subject to these restrictions, we may neglect variations in c_L with elongation and may interpret c_L (in calories per gram per ° C) as being identical with c_p (in calories per gram per ° C) at the same temperature.

4. Accurate knowledge of c_L is needed for the correlation of the reversible heat developed when rubber is stretched rapidly with the entropy component of the stress-strain curve. It is also needed to correlate calculated energy losses with rise in temperature in flexometer experiments.

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GELATION OF RUBBER SOLS BY ULTRAVIOLET LIGHT *

R. BUCKINGHAM AND G. V. PLANER

DEPARTMENT OF CHEMISTRY AND RUBBER TECHNOLOGY, NORTHERN POLYTECHNIC, LONDON, ENGLAND

On exposure of rubber sols to ultraviolet light in the absence of oxygen, gels known as rubber photogels are formed under certain conditions. It has been found that on removing the solvent the rubber recovered exhibits properties somewhat similar to those obtained on vulcanization.

The study of photogelation is of interest, apart from the purely theoretical aspect, because of its possible bearing on the problem of vulcanization, including the various sulfurless vulcanization reactions. Another important aspect is the bearing on the study of the aging of rubber, as well as on the industrial manufacture of rubber cements and solutions.

Solvents used in the preparation of photogels are divided into active ones, *i.e.*, those which condense with the rubber on irradiation, and nonactive ones. A number of accelerators are effective in the reaction; among the most efficient of these are carbonyl compounds such as benzophenone, acetone, benzaldehyde, as well as benzoquinone, chloranil, eosin, etc.

The nature of the reaction has not hitherto been satisfactorily explained, and a number of widely varying theories have been advanced in the literature. Some investigators regard the reaction as being a polymerization. Pummerer and Kehlen[1] support this view because of the similarity to the photopolymerizations of styrene and isoprene, both of which are favored by the same accelerators as those used in the formation of photogels. Stevens[2], on the other hand, mentioned cyclization of the rubber molecules as a possible mechanism, and Asano[4] drew attention to the possibility of a stereochemical rearrangement taking place in the molecule on irradiation, producing insolubility.

In the experimental work to be described, the reaction was studied by determining the reaction curves under various conditions. As it has frequently been pointed out in the literature that inconsistent quantitative results have been obtained in the study of this reaction, particular importance was attached to developing methods which enabled reproducible results to be obtained.

EXPERIMENTAL

The experimental method relied in principle on irradiating sample solutions of various concentrations of rubber and accelerator, and following the viscosity changes for each solution up to gelation by the use of the rolling ball method.

(1) *Preparation of Sample Tubes.*—A weighed sample of pale crepe rubber previously extracted in acetone, in the dark, as well as a small, weighed steel ball were placed in a glass tube of known weight carrying a delivery tube at one end. The accelerator was then weighed out and dissolved in 30 to 37 cc. of

* Reprinted from the *Translations of the Institution of the Rubber Industry*, Vol. 21, No. 3, pages 175–187, October 1945.

purified carbon tetrachloride. The solution was transferred quantitatively to the sample tube and the delivery tube was connected to the water pump. The liquid was then allowed to boil under reduced pressure for 25 minutes, when the delivery tube was sealed off. In this way the air over the liquid, as well as that held by the rubber and dissolved in the solvent, was removed. On weighing the tube and contents together with the piece of delivery tube removed, the weight of solvent was determined, and hence the concentration of the sol calculated. The tubes were subsequently placed in an automatic shaker maintained at 100° C and shaken for not less than 12 hours. Further shaking was found to have no effect on the viscosities.

In this way two sets of sample solutions were prepared, the rubber contents ranging from 0.5 to 0.65 per cent by weight. The solutions of one of the sets were made up with 20 per cent of accelerator, those of the other with 30 per cent, with respect to the weight of rubber.

The accelerator used was benzophenone, as this is readily soluble in carbon tetrachloride, is an efficient accelerator for the light reaction, and does not promote vulcanization of the rubber in the dark.

(2) *Method of Irradiation.*—Irradiation was carried out by means of a mercury vapor lamp placed at a distance of 11.5 cm. above the tubes. To ensure completely homogeneous gelation of the solutions, an apparatus was constructed enabling the tubes to be continuously rotated in a horizontal plane about their longitudinal axis during exposures, the rate of rotation being 100 revolutions per minute. To avoid warming of the solutions, irradiation was carried out in doses not exceeding five minutes at a time, viscosity measurements being taken at various time intervals.

The sample tubes were of length 31 cm., internal diameter 1.35 cm., and consisted of glass of 1 mm. thickness.

(3) *Viscosity Measurements.*—The method used for the viscosity determinations relied on the measurement of the time required for a steel ball to roll through a given distance down an inclined tube containing the solution. This method has a number of advantages over the use of the Ostwald or Ubbelohde viscometers for the present purpose; the method is a continuous one; it is applicable over a fairly wide range of viscosities, and the rubber solution is not in contact with air during the viscosity determination. This last condition is of importance, as most accelerators used in the preparation of photogels also promote the degradation of rubber sols in the presence of oxygen.

The principle involving the measurement of rolling times at a fixed angle for viscosity determinations has been known for some time, and was first described by Flowers[4]. For the present purpose the method had to be modified to enable measurements to be carried out over a wide range of viscosities. The relationship between the angle of inclination of the tube, θ, and the rolling time, T', for a given distance, was therefore determined. For the viscosity measurement of any particular solution, the angle of tilt could then be adjusted so that T' would have a value which could be conveniently measured with a stop watch. The relation between θ and T' being known, the rolling times corresponding to different viscosities could thus be correlated.

Construction of the Rolling Ball Viscometer.—Figure 1 shows diagrammatically the apparatus constructed for the viscosity determinations. A is a metal plate whose upper and lower edges, FG and HJ, respectively, were machined to be accurately parallel. Plate A is hinged to cross bar B at C. The tube containing the rubber solution was held in position by means of the two semi-circular brakets, E, and clamping ring K. Plate A could be locked

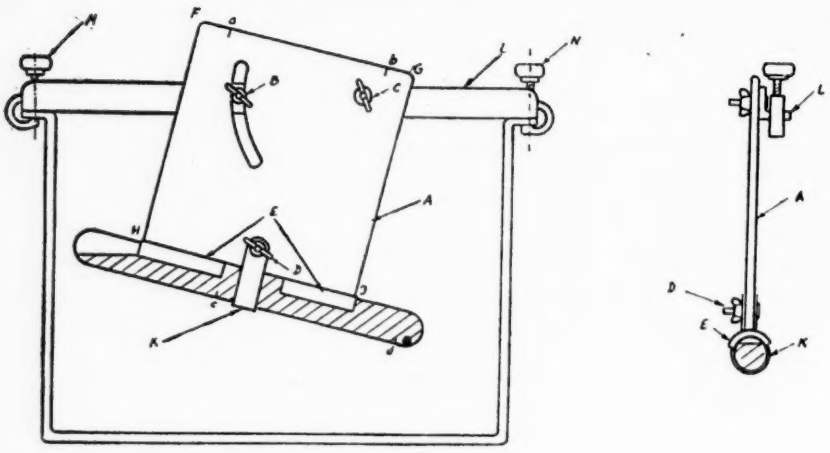


FIG. 1.

into position at different angles of tilt by means of wing nuts B and C. Cross bar L was screwed on to the rim of the thermostat bath by means of clamps M and N. Two marks, *a* and *b*, were made at the top edge of Plate A, at a distance of 11.40 cm. from each other. By means of a cathetometer placed opposite the apparatus, the difference in height between *a* and *b* was determined in each case. The sines of the angles of inclination of the tube could therefore be determined.

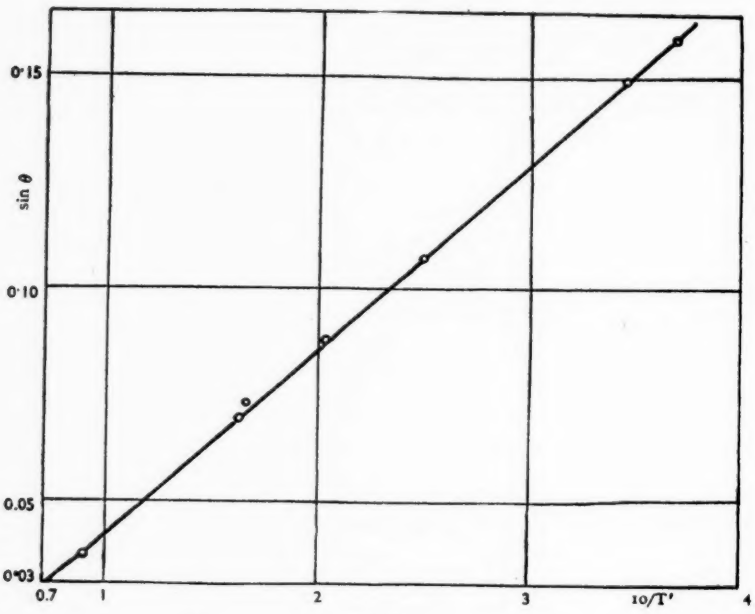


FIG. 2.

The rolling time, T', was measured as follows: The small steel ball contained in the sample tube was taken to the upper end of the tube by means of a magnet. It was then released and allowed to roll down the tube. The time taken by the ball to pass from mark *c* to mark *d* was measured with a stop watch, the tube being observed through a window in the thermostat bath.

Calibration of the Rolling Ball Viscometer.—A number of sample tubes, each containing rubber solutions as well as a small steel ball, were prepared. The steel balls were of the type used in ball bearings. They are obtainable at very small tolerances, and those selected for use were of diameter 4 mm. and weighed 0.2545 gram ± 0.0003 gram. The internal diameter of the tubes was 1.35 cm. and their length approximately 31 cm. To establish the relationship between θ and T', one of the sample tubes was clamped into position; the times taken for the sphere to roll from *c* to *d* were measured for various angles of inclination. The distance between *c* and *d* was 17 cm., the marks being

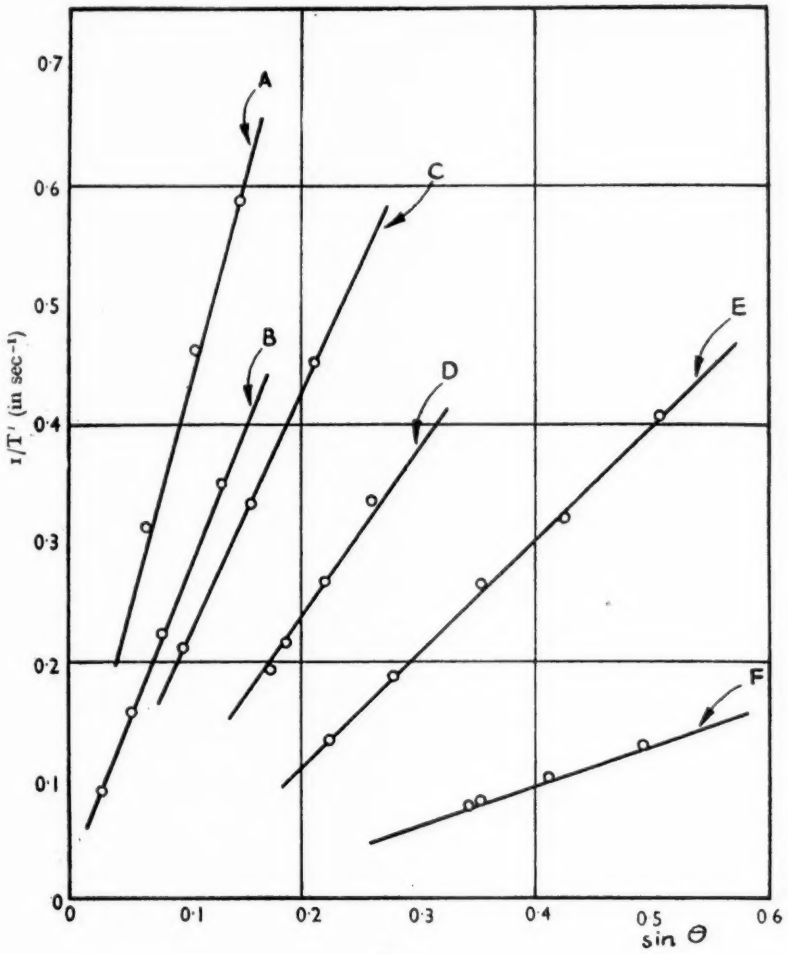


FIG. 3.

arranged so that the ball attained constant velocity before reaching *c*. T' was obtained by taking the mean of a number of readings of the rolling time for each angle of inclination. The individual readings were in good agreement with each other.

The relationship between sin θ and $1/T'$ was found to be linear (Figure 2). It was thus possible to use the slope of the graph connecting sin θ and $1/T'$ as a measure of viscosity. The calibration was therefore carried out as follows:

The sample tubes prepared as described above were subjected to different periods of irradiation, corresponding to various stages in the gelling reaction. The sin θ — $1/T'$ curves were then determined for the solutions by means of the rolling-ball viscometer (Figure 3).

The tubes were now successively opened and the solutions transferred to an ordinary Ubbelohde viscometer attached to a variable pressure system. The time, T, for the level of the solution in the viscometer to fall through a fixed distance was then determined at various pressures, P, for each solution (Figure 4). As the rubber solutions used here did not contain an accelerator,

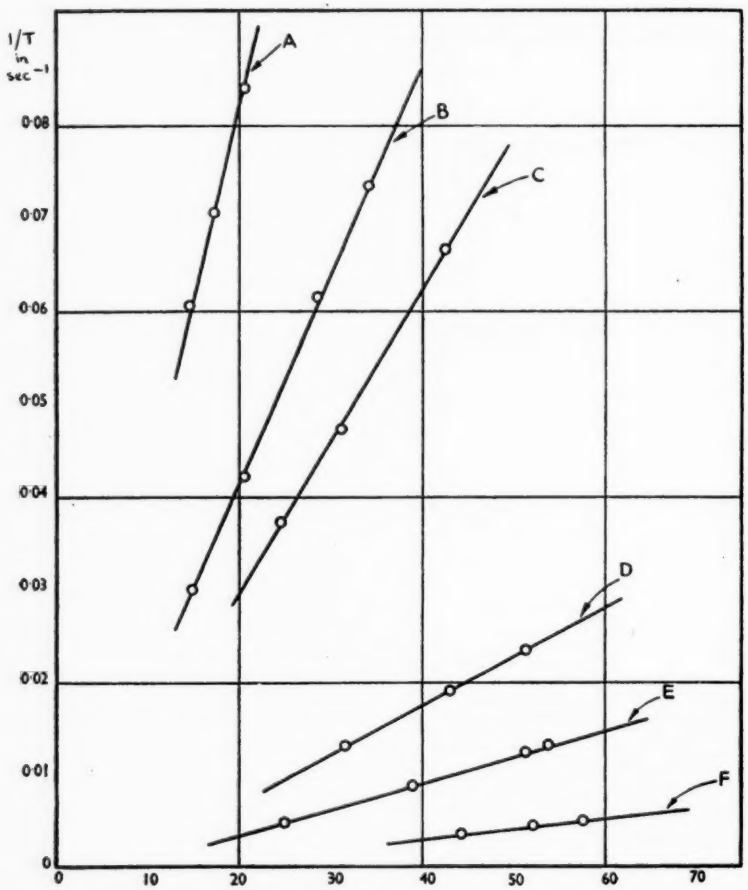


FIG. 4.

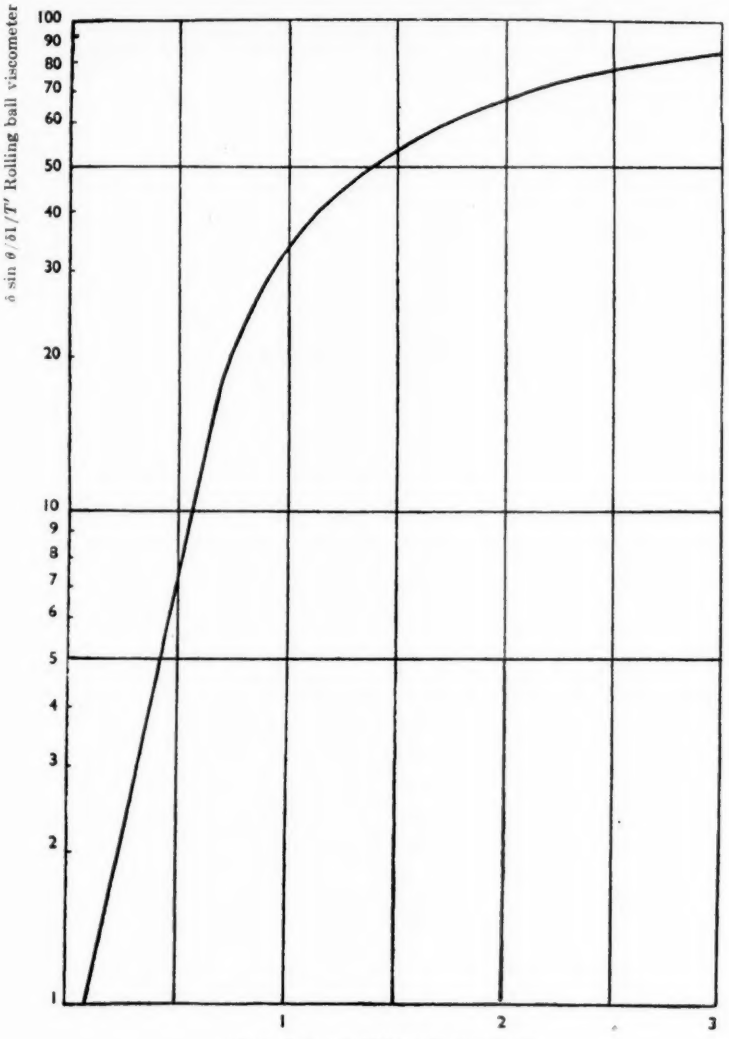
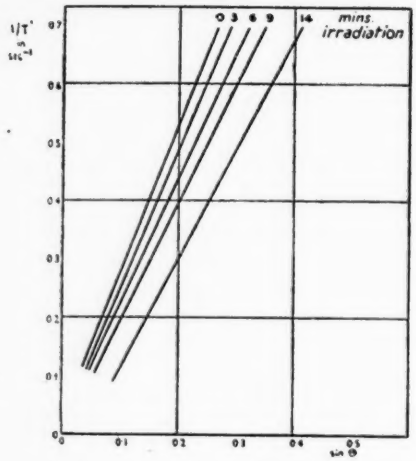


FIG. 5.

the degradation due to air of the solution in the viscometer was too slow to affect the readings.

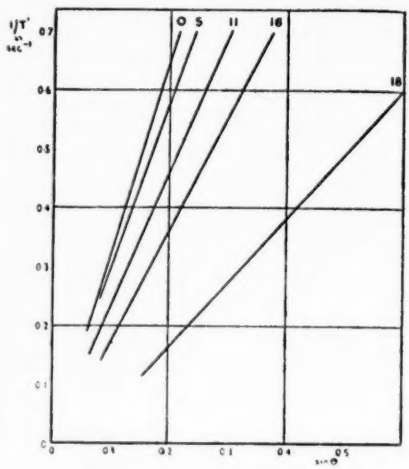
Figure 5 shows the calibration curves connecting the reciprocals of the slopes, $\delta \sin \theta/\delta 1/T'$ for the rolling-ball viscometer, and $\delta P/\delta 1/T$, determined with the Ubbelohde viscometer. This enabled measurements obtained with the rolling-ball viscometer to be expressed in terms of the "incremental rate of flow" as a function of pressure, $\delta P/\delta 1/T$, which is very nearly proportional to the viscosity.

To establish a reference standard, the value of $\delta P/\delta 1/T$ was determined for water, and was found to be 71.0. Measurements on rubber solutions may therefore be referred to this value.



Solution G. Concentration 0.600%.

FIG. 6.

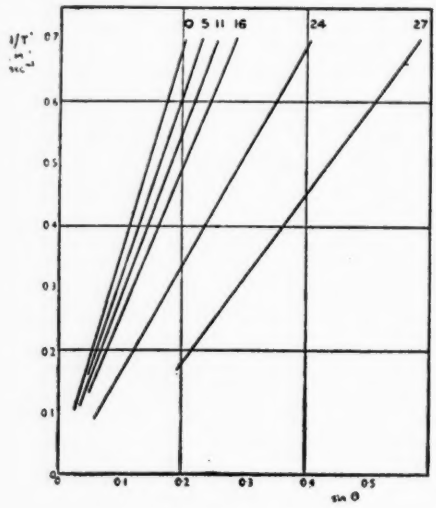


Solution H. Concentration 0.572%.

FIG. 7.

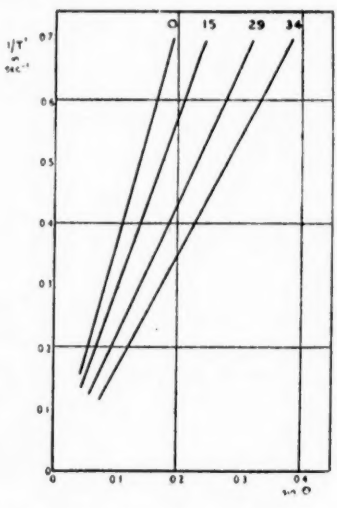
Measurements on Rubber Sols containing Benzophenone.—Two preliminary experiments were carried out on solutions prepared as described in Section 1 to determine whether any viscosity changes occurred in a solution which had not been irradiated, on standing, when protected from light, and whether any growth in the dark took place after irradiation.

The viscosity of a solution containing 0.5 per cent of rubber and 20 per cent of benzophenone was found to remain unchanged on standing in the dark for several weeks.



Solution I. Concentration 0.525%.

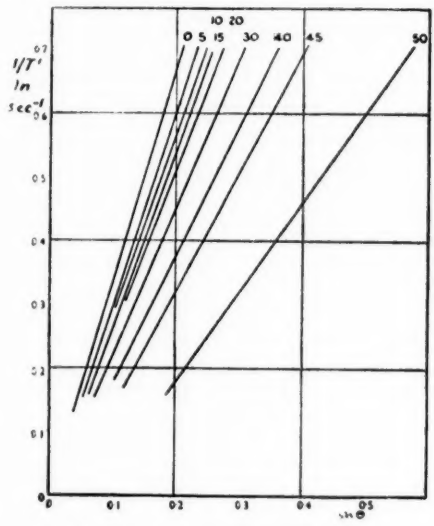
FIG. 8.



Solution K. Concentration 0.510%.

FIG. 9.

Viscosity measurements were carried out on a solution immediately after a short period of irradiation. The tube was then allowed to stand for several days, protected from light, when measurements were repeated. The viscosity was again found to be unchanged, showing that no dark-growth had taken place during the period of standing.



Solution L. Concentration 0.500%.

FIG. 10.

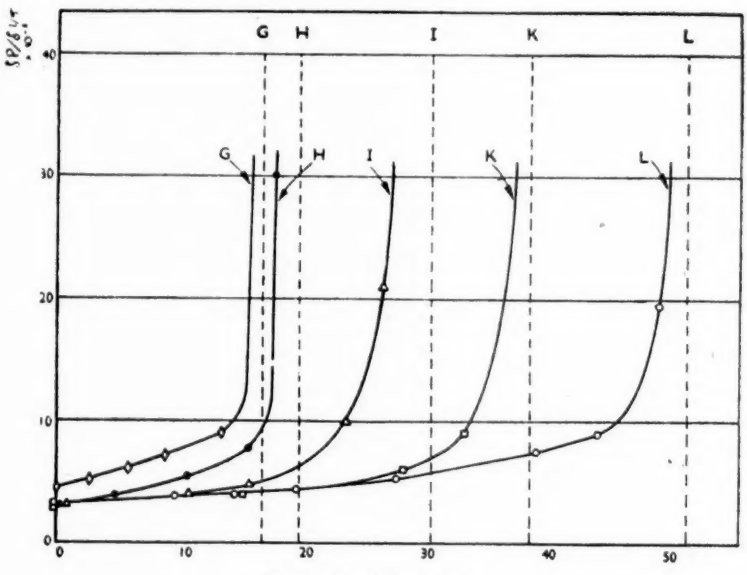
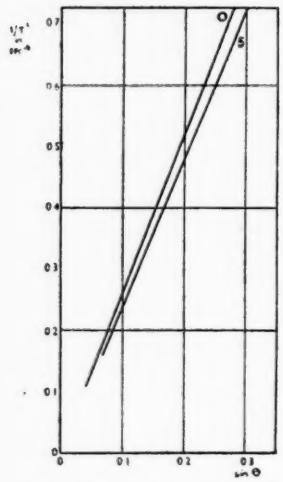
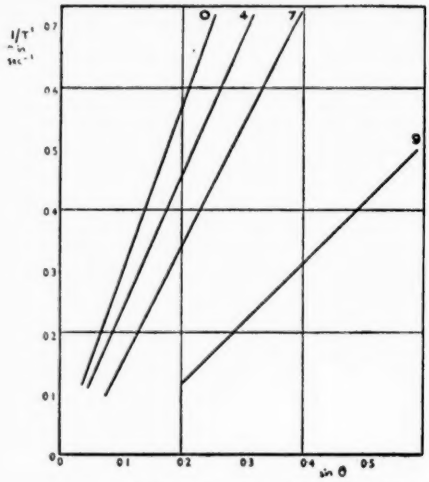


FIG. 11.—Reaction curves 20% accelerator.



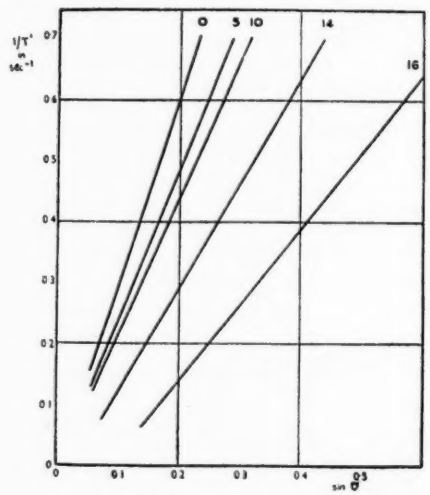
Solution M. Concentration 0.636%.

FIG. 12.



Solution N. Concentration 0.572%.

FIG. 13.



Solution O. Concentration 0.546%.

FIG. 14.

The sample solutions made up with accelerator were now successively irradiated, as described in Section 2, and the curves showing the relation of $\sin\theta$ to $1/T'$ were determined from time to time. T' was in each case obtained by taking the mean of three readings of the rolling time. All viscosity measurements were carried out at 25° ± 0.1° C.

In addition to the viscosity determinations, the times of irradiation at which gelation just commenced were noted for each solution. These gelling times were fairly well defined as will be seen in the following.

Figures 6 to 10 and 12 to 14 show the curves corresponding to varying periods

of irradiation, for each of the solutions examined. Solutions G, H, I, K and L were made up with 20 per cent of benzophenone, M, N and O contained 30 per cent of the accelerator, with respect to the weight of rubber.

The reciprocals of the slopes, $\delta \sin \theta/\delta 1/T'$, were measured for each of the above curves. The corresponding values of $\delta P/\delta 1/T$ were then derived by means of the calibration curve (Figure 5). The reaction curves were obtained by plotting $\delta P/\delta 1/T$ against the corresponding times of irradiation, for each solution. Figures 11 and 15 show the reaction curves for the sets of solutions containing 20 and 30 per cent of accelerator, respectively. The times of irradiation at which gelation just set in are indicated by dotted lines.

The relationship between the gelling times and rubber contents is shown in Figure 16 for the two sets of solutions.

(4) *Discussion of Results.*—Considering at first the graph connecting rubber contents and gelling times (Figure 16), it will be seen that, especially in the

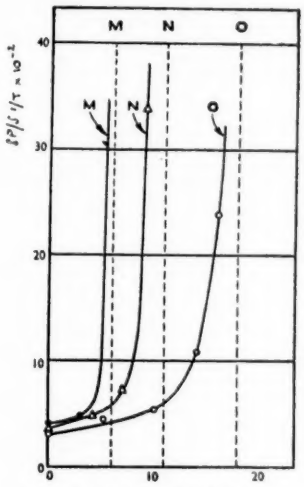


FIG. 15.—Reaction curves, 30% accelerator.

lower viscosity region, the gelling times vary considerably for small changes in concentration. At lower concentrations the curves flatten out and approach asymptotically a constant value of concentration. The latter represents the minimum rubber content necessary to effect gelation for the particular type of rubber used.

It has frequently been reported in the literature that inconsistent gelling times were obtained in the absence as well as presence of accelerators. It is therefore possible that this may in some cases have been due to the fact that the considerable influence of concentration on the reaction rate was not taken into account.

It is also of interest to note that the rate of reaction increases with an increase in concentration of the accelerator, even at concentrations as high as 20 to 30 per cent, as shown by the curves in Figure 16. It is thus apparent that fairly large quantities of benzophenone take part in the reaction.

At lower rubber contents the two curves in Figure 16 approach each other,

indicating that the quantity of accelerator used has probably no appreciable effect on the minimum rubber content required for gel formation.

In all cases the slope of the reaction curves (Figures 11 and 15) increases at first slowly until a certain critical value of the viscosity, expressed by $\delta P/\delta 1/T$ is reached. No initial thinning of the solutions as has been observed in the absence of accelerators took place before gelation[5]. (Planer, Thesis, Lond. Univ., 1945). After the critical extent of the reaction is attained the viscosity suddenly increases rapidly until gelling takes place.

The general shape of the reaction curves is characteristic of three-dimen-

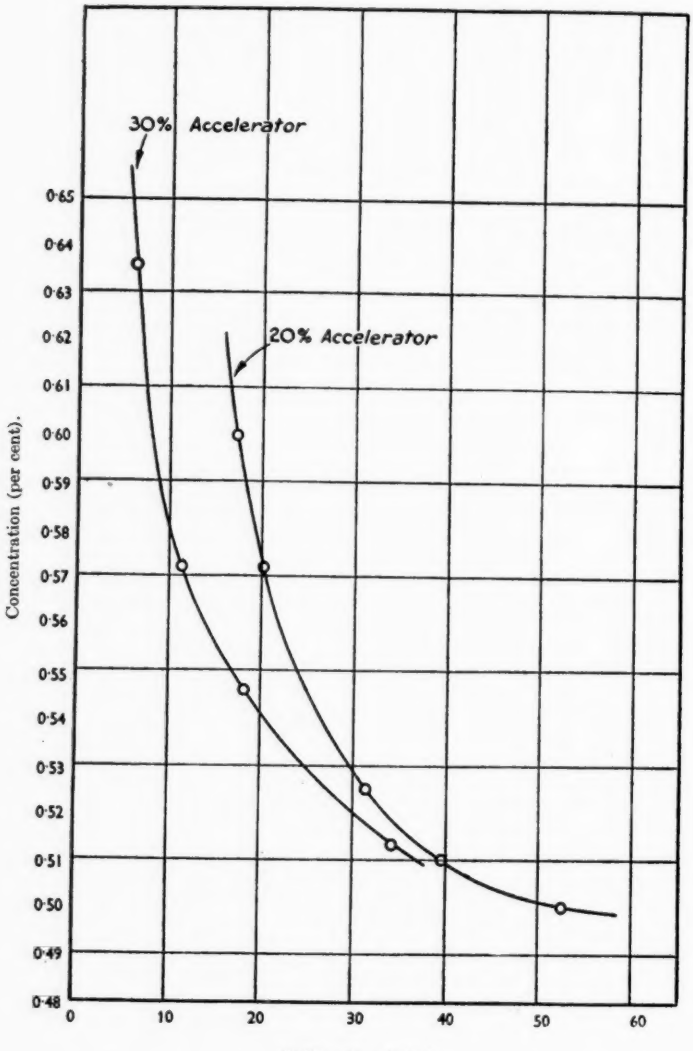


FIG. 16.—Relationship between gelling time and rubber content.

sional polymerization reactions, the above behavior leading to the formation of gelled or insoluble products being known as a criterion of this type of reaction[6].

Thus, on commencing irradiation, intermolecular linkages are formed between the rubber chains. The reaction proceeds at first slowly, as indicated by the initial gradual rise of the reaction curves. When a certain critical number of linkages has been formed, that is, on reaching the sharply defined turning points shown by the curves, further irradiation results in the formation of large molecules, causing the rapid increase in viscosity and subsequent solidification. The rapid growth of molecules which sets in after a certain critical extent of the reaction has been reached may be ascribed to the enhanced capacity for further growth of the larger molecules, due to their great number of unreacted end groups.

A further characteristic of three-dimensional polymerizations is the fact that the previously mentioned critical extent of the reaction is independent of the amount of catalyst used. It may be seen from Figures 11 and 15 that this condition is also satisfied. The critical values of $\delta P/\delta 1/T$ are the same order of magnitude for the solutions containing 20 per cent and 30 per cent of accelerator, as well as for the individual solutions of each set, having slightly different rubber contents. It may therefore be seen that the small differences in concentration of solutions G to L and M to O are insufficient to affect appreciably the critical extent of the reaction which has to be reached before the formation of large molecules can set in. These differences in concentration have, however, a considerable influence on the time required for the attainment of this critical extent.

From the above considerations one is therefore reasonably justified in concluding that the reaction has in fact mainly a three-dimensional polymerization mechanism.

In a recent paper, Stevens[2] pointed out that photogelation may be due to the formation of an insoluble rubber product or modification, and he drew attention in particular to the possibility that the reaction may possess a ring formation. This explanation is not supported by the present data, as the curve for this type of reaction would be substantially a linear one. It is, however, probable that a small amount of cyclization takes place in conjunction with the three-dimensional polymerization.

The photogelation reaction bears a certain resemblance to the heat vulcanization of rubber by means of benzoyl peroxide, which possesses a polymerization mechanism. The reactions are thus both three-dimensional polymerizations and are generally accompanied by the addition of organic fragments to the rubber. In both cases the unsaturation of the products is but slightly lower than that of the untreated rubber.

In the benzoyl peroxide reaction, benzoate and phenyl radicals are formed by the action of heat, and are known to enter the composition of the rubber molecules. It appears possible that in the photogelation reaction radicals are formed from the solvent and accelerator molecules by the action of ultraviolet light. These promote the formation of intermolecular linkages and attach themselves to the rubber.

Farmer[7] suggested that the interlinking of different rubber units in the benzoyl peroxide reaction may take place by the formation of carbon-to-carbon bonds at the α-methylenic groups. Phenyl and benzoate groups are further thought to enter the composition of the rubber by substitution, mainly at the α-methylene groups adjacent to the methyl groups in the rubber chains. It

appears therefore possible that in the case of photogelation the reaction may proceed in a similar manner.

The products obtained by irradiation of rubber sols in inactive solvents, *i.e.*, without noticeable additions of organic fragments, do not differ fundamentally from those produced with active solvents. Similarly, the choice of accelerator does not have a marked effect on the properties of the gels. The above incorporation of organic fragments is therefore of less importance, whereas three-dimensional polymerization is the main factor determining the gelation of rubber sols by ultraviolet light.

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THE PHOTOGELATION OF RUBBER SOLS IN THE ABSENCE OF ACCELERATORS *

R. Buckingham and G. V. Planer

Irradiation of rubber sols with ultraviolet light in the absence of oxygen results in gelation under certain conditions[1]. From a study of the reaction curves the mechanism of this reaction was shown by the authors in a previous paper[2] to consist mainly of a three-dimensional polymerization. The curves were derived by following the reaction by means of viscosity measurements, in the presence of an accelerator, benzophenone, with carbon tetrachloride as solvent.

It was deemed of interest to compare these curves with those obtained without the use of benzophenone, and the experimental work described in the following deals with the study of the reaction in the absence of accelerators.

The products obtained on removing the solvent from photogels differ markedly for various solvents, but are in all cases insoluble and show elastic properties similar to those of lightly vulcanized rubber.

The solvents used are of two types, active and inactive. In the case of the active ones, such as carbon tetrachloride, the solvent molecules condense with the rubber, and on removal of the solvent from the resulting photogels, the products are often considerably heavier than the original rubber samples. When carbon tetrachloride is used, the reaction product has been shown to contain appreciable amounts of combined chlorine. With inactive solvents like benzene, ligroin, etc., no increases in weight are observed and gels are generally formed less readily.

EXPERIMENTAL

The experimental method employed relied in principle on viscosity measurements on a number of sample solutions of equal concentration, which were exposed to the mercury vapor lamp for varying periods of time. The measurements were carried out on several sets of such solutions derived from a number of mother solutions.

Attention has been drawn in the literature to the fact that widely varying results have been obtained under apparently identical conditions in the study of this reaction. These inconsistencies are believed by some investigators to be due to the presence of traces of oxygen or other impurities in the solutions. A number of different experimental methods were, therefore, tried to overcome this difficulty, and results of satisfactory consistency were obtained with the procedure described below.

Preparation of sample tubes.—Pale crepe rubber was extracted with acetone, with care taken to shield the extractor from light. It was then dried by placing it in a desiccator and evacuating till free from acetone.

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* Reprinted from the *Journal of the Society of Chemical Industry*, Vol. 65, No. 1, pages 6–8, January 1946.

Purified carbon tetrachloride was used as solvent, and was obtained by allowing B.P. carbon tetrachloride to stand over anhydrous sodium sulfate for several days, decanting, and distilling at 77° C.

A weighed sample of rubber was placed in a glass tube of known weight, to which a narrow delivery tube was attached at one end, and approx. 60 cc. of carbon tetrachloride was added. The air was then removed by allowing the solvent to boil under reduced pressure for 20 minutes, when the tube was sealed off. On weighing the tube and contents, the weight of carbon tetrachloride and hence the concentration of the sol was determined.

The rubber was dispersed by shaking the tube for a minimum of 24 hours in an automatic shaker, maintained at about 100° C by means of boiling water. The viscosities of the sols obtained were found to vary only with the concentration, and to be independent of the time of shaking in excess of the above period.

A number of such tubes were prepared, and from each of these mother solutions five smaller sample tubes were made up. The transfer of the solutions was carried out under rigorous exclusion of air, by means of the apparatus shown diagrammatically in Figure 1.

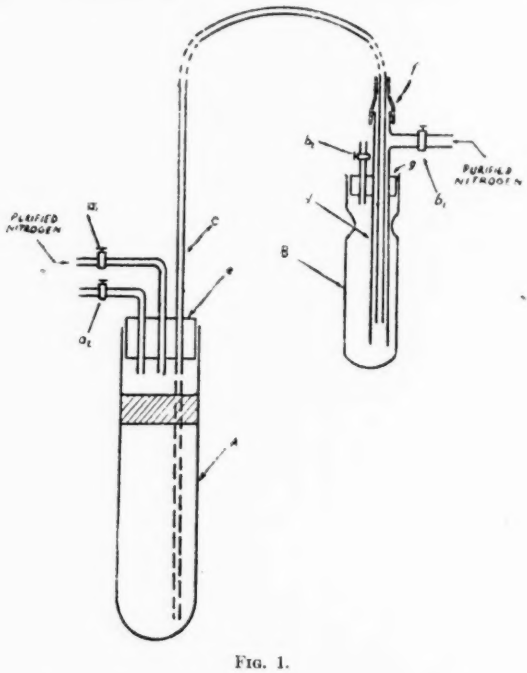

FIG. 1.

The tube containing the mother solution was opened by filing a ring near its upper end and removing the top cone. Stopper *e* was then rapidly pressed into position, as shown in Figure 1. Meanwhile, a slow stream of purified nitrogen was passed into tube A through a_1, leaving the system at b_2, taps a_2 and b_1 being closed. In this way the air was swept out of tube A and the delivery tube *c*. After approximately five minutes, taps a_2 and b_1 were opened and nitrogen was passed through tubes A and B for several minutes. Tube *c*

was then lowered until it almost touched the bottom of tube A, as indicated by dotted lines in Figure 1, tap a_2 being now shut and b_1 partially shut. The pressure built up in tube A then drove part of the solution into tube B.

To prevent blockage of tube *d* by the rubber solution, it was raised slightly by sliding it upwards together with rubber sleeve *f* which served as an air-tight seal. As the rubber solution flowed into tube B, the latter was slowly lowered by sliding it down together with stopper *g*. When approximately 9 cc. had collected, taps a_2 and b_1 were fully opened, b_2 and a_1 being partially closed. The rubber solution remaining in delivery tube *c* was thus driven back into tube A. Tap b_2 was then fully opened and tube *d* lowered again by means of rubber sleeve *f*. The stream of nitrogen issuing from it therefore prevented air from diffusing into tube *c* after removing sample tube B. The latter was finally sealed off at the constriction and removed. Four further sample tubes were then filled in this way from the same mother solution contained in tube A. Tube *c* had, of course, to be swept out only before filling the first sample tube.

It will be seen that, during the procedure described above, only the surface of the rubber solution in tube A came in contact with air for a few seconds while pressing stopper *e* into position. The top layer of the solution, shown shaded in Figure 1, which may have contained absorbed oxygen, was therefore discarded.

In this way a number of sample tubes containing rubber sols of equal concentration were prepared, and the procedure was repeated for several mother solutions.

The purification of the nitrogen was carried out as follows. Commercial nitrogen was passed through an alkaline pyrogallol solution consisting of 160 parts of potassium hydroxide, 8 parts of pyrogallic acid and 120 parts of water, by weight, and thence over copper turnings contained in a copper tube heated to approx. 500° C to remove oxygen. It was dried by passing through a wash-bottle containing concentrated sulfuric acid and a calcium chloride tower. The nitrogen stream was finally divided into two branches, one of which supplied tube A, the other tube B (Figure 1). Each of these comprised a wash-bottle containing purified carbon tetrachloride, through which the nitrogen had to pass before entering tubes A and B. This prevented any appreciable amount of solvent from being carried away by the nitrogen, and also provided a means of checking the rates of gas flow.

Irradiation.—The sample tubes were irradiated for varying periods of time by placing them horizontally under a quartz mercury vapor lamp having an arc 8 cm. long, and operating at a tension of 15 volts. The power dissipation was 38 watts. Irradiation was carried out in doses not exceeding ten minutes at a time to prevent warming of the solutions. The tubes were placed at a distance of 11.5 cm. from the lamp, and consisted of glass of 1 mm. thickness; their internal diameter was 1.3 cm. and their lengths about 13 cm.

Viscosity measurements.—The viscosity measurements were carried out by means of an Ubbelohde viscometer to which a variable pressure system was attached. Readings were taken of the times, T, required for the level of the rubber sol in the viscometer to fall through a given distance for different pressures, P, in the case of each solution examined. All viscosity determinations were carried out at 25° ± 0.1° C.

During the above measurements, the rubber solutions in the viscometer were exposed to air. The degradation due to oxygen was, however, found to be too slow to affect the readings, in the case of solutions containing no accelerator.

As a preliminary experiment, rubber solution No. 1 was divided into two portions, one of which was irradiated until its viscosity had increased somewhat. The times of flow for various pressures were then determined for both the irradiated and untreated portions. On plotting 1/T against P, straight lines were obtained in both cases (Figure 2). It may therefore be seen that the

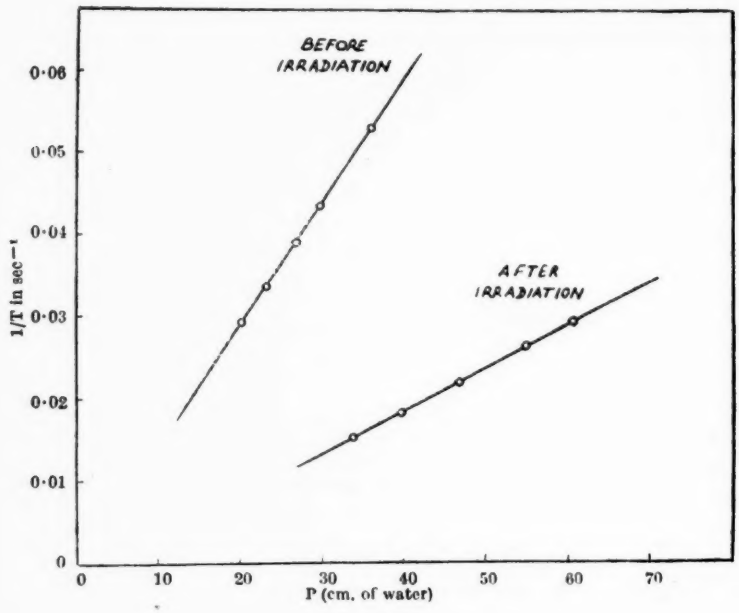

FIG. 2.

structural viscosity effect was negligible for the range of pressures used.

Solutions No. 2 and No. 3 containing 1.24 and 1.28 per cent of rubber, respectively, were prepared, and from each of these a set of sample tubes was made up in the manner described previously. Four tubes of each set were then exposed to the mercury vapor lamp for varying periods of time, as described above, one of each being irradiated until gelation just set in, and one

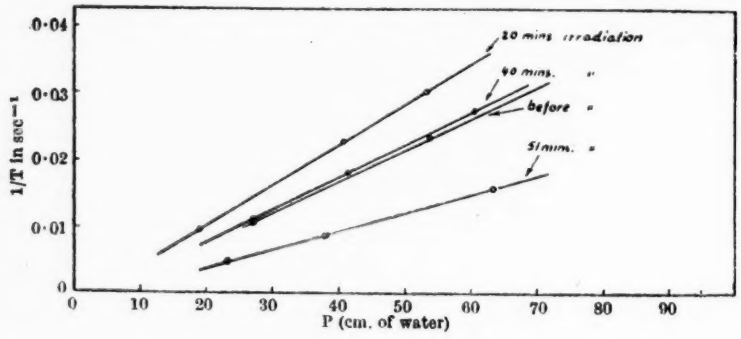

FIG. 3.

being retained for viscosity measurements on the untreated solution. The tubes were then opened and the solutions transferred to the viscometer. The times of flow, T, for various pressures, P, were then determined and the pressures plotted against the reciprocals of the times (Figure 3 and 4). The reaction curves were derived by measuring the reciprocals of the slopes of the

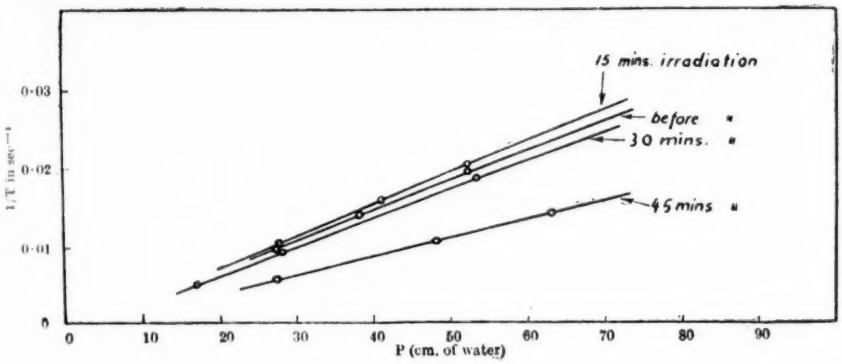

FIG. 4.

straight lines so obtained, $\delta P/\delta 1/T$, and plotting them against the corresponding times of irradiation (Figure 5).

Alternatively, reaction curves can be obtained by plotting the times of flow at one particular pressure against the time of irradiation. However, the extensions of the P–$1/T$ curves are found not to pass through the origin in

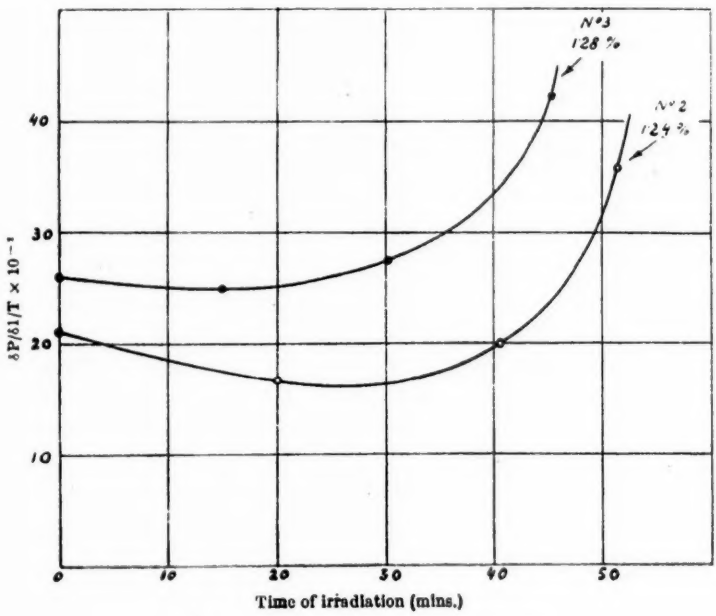

FIG. 5.—Reaction curve; no accelerator present.

most cases, but to intercept the P-axis near the origin. The incremental rate of flow as a function of pressure, $\delta P/\delta 1/T$, which remains constant over the measuring range for each solution and which is nearly proportional to the viscosity, was therefore considered more significant. The gelling times of solutions 2 and 3, that is, the times of irradiation at which solidification just set in, were 58 and 51 minutes, respectively. Gelling times obtained for further solutions of very nearly the same concentration were in good agreement with the above results.

Figure 6 shows the type of reaction curve which was obtained in the presence of an accelerator, benzophenone. A different experimental procedure from that given above had to be employed for the study of photogelation in the presence of accelerators, and this is described in a previous paper[2].

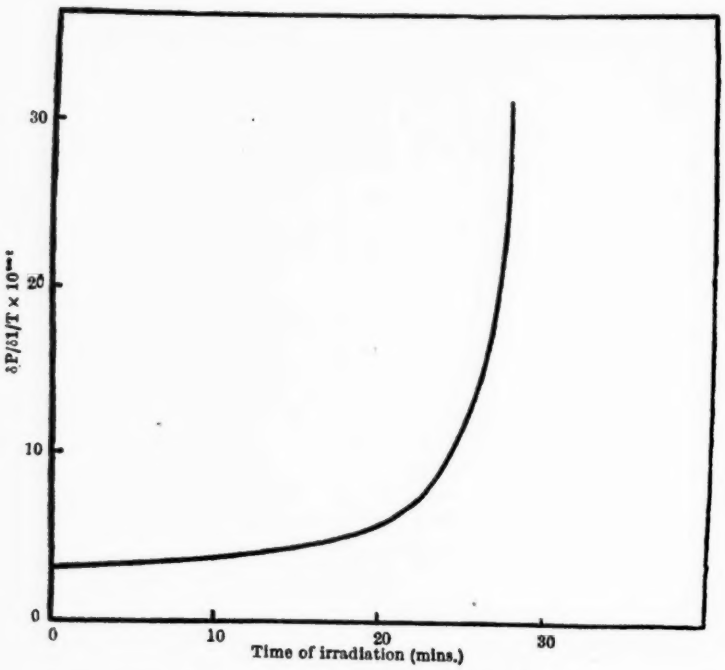

FIG. 6.—Reaction curve; accelerator present
Rubber content: 0.5%. Accelerator content: 20% of the weight of rubber.

As a comparison the P–$1/T$ curve for water was determined by means of the same viscometer under identical conditions to those of the measurements on the rubber solutions. The value of $\delta P/\delta 1/T$ for water was found from the graph to be 71.0.

Discussion of results.—It may be seen from the reaction curves in Figure 5 that the viscosity of the solutions containing no accelerator decreased initially on irradiation. This may be ascribed to degradation due to oxygen, traces of which may be present as an impurity. Oxidation cleavages are probably at first produced in the rubber chains, preceded by hydroperoxide formation.

The reaction curve obtained in the presence of benzophenone (Figure 6)

is fundamentally of the same type as those determined in its absence, the initial degradation, however, being prevented by the accelerator. In the presence of benzophenone, the slope of the reaction curve rises at first slowly. After reaching a certain critical value, the viscosity suddenly increases rapidly until gelling takes place. This type of curve is characteristic of three-dimensional polymerizations[3], and it may therefore be seen that the reaction proceeds by a similar mechanism also in the absence of benzophenone. Thus, in the latter case, the rubber chains are at first broken up into smaller units. When all the free oxygen has been used up, these interlink forming a three-dimensional network. On gelling the substance need, of course, not be bound into a single molecule. Smaller units may still be present within the network of large molecules. This would explain the fact that small portions of soluble material can be extracted from photogels.

It appears possible that the interlinking of rubber units may take place in a manner similar to that proposed in the case of the heat polymerization of rubber sols by means of benzoyl peroxide[4]. Radicals may be produced from the solvent, or accelerator, if present, by the action of ultraviolet light. These promote the formation of carbon-to-carbon bonds at the α-methylene groups between different rubber units. Cross-linked structures will, therefore, be formed of the type:

$$\begin{array}{l} \text{—CH—CCH}_3\text{=CH—CH}_2\text{—} \\ \quad\quad | \\ \text{—CH—CCH}_3\text{=CH—CH}_2\text{—} \end{array}$$

and to a lesser extent:

$$\begin{array}{l} \text{—CH—CCH}_3\text{=CH—CH}_2\text{—} \\ \quad\quad | \\ \text{—CH—CH} \quad \text{=CCH}_3\text{—CH}_2\text{—} \end{array}$$

In addition, organic fragments, R, derived photochemically from the solvent or accelerator may attach themselves to the rubber by substitution, mainly at the α-methylene groups adjacent to the methyl groups in the rubber chains, as follows:

$$\begin{array}{l} \text{—CH—CCH}_3\text{=CH—CH}_2\text{—} \\ \quad\quad | \\ \quad\quad \text{R} \end{array}$$

The ease with which further cross-linking takes place is influenced by the nature of group R.

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[2] Buckingham and Planer, *Trans. Inst. Rubber Ind.* **21**, 175 (1945).
[3] Flory, *J. Am. Chem. Soc.* **63**, 3083 (1941); Stockmayer, *J. Chem. Phys.* **11**, 45 (1943); **12**, 125 (1944).
[4] Farmer, *Trans. Faraday Soc.* **38**, 340 (1942); Buckingham and Planer, *Trans. Inst. Rubber Ind.* **21**, 175 (1945).

NONSULFUR VULCANIZATION. II. AN EXPERIMENTAL STUDY*

TURNER ALFREY

BROOKLYN POLYTECHNIC INSTITUTE, BROOKLYN, N. Y.

J. G. HENDRICKS

NATIONAL LEAD CO., BROOKLYN, N. Y.

ROBERT M. HERSHEY

BARRETT DIVISION, ALLIED CHEMICAL AND DYE CORP., EDGEWATER, N. J.

AND

HERMANN MARK

BROOKLYN POLYTECHNIC INSTITUTE, BROOKLYN, N. Y.

In Part I[1] the literature on nonsulfur vulcanization was reviewed, with particular emphasis on the reaction mechanisms involved. The present paper reports a series of experiments conducted in this laboratory. The first part deals with a chemical investigation of dinitrobenzene vulcanization; the second part deals with the physical properties of nonsulfur vulcanizates, and includes some results reported in the literature as well as those experimentally established here.

CHEMICAL INVESTIGATION OF DINITROBENZENE VULCANIZATION

Discussion of Results.—Wright and Davies[2] have shown that when rubber is vulcanized in solution with dinitrobenzene, either water or litharge and fat acid (which form water) must be present for gelation to occur. Furthermore to make hard rubber with dinitrobenzene, both water and litharge must be added to the dry rubber. No prior work has been carried out with fat acid-free rubber in investigating nitrobenzene vulcanization of dry rubber in the soft rubber stages, but it has been generally assumed that the results of vulcanization in solution may be applied to "dry" rubber vulcanization. We have now investigated this point, obtaining results which are not in agreement with the above assumption. We find that fat acid or water is not necessary for the vulcanization of "dry" rubber by nitrobenzene in the soft rubber stages.

The course of the vulcanization reaction was traced by following changes in unsaturation and in physical properties of the rubber. Since direct addition of water to rubber might lead to questionable results because of solubilities and temperatures encountered, it was considered best to control the amount of water present through the addition of litharge and fat acid to extracted rubber.

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* Reprinted from the *India Rubber World*, Vol. 113, No. 5, pages 653–658, February 1946.

[1] Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

[2] National Lead Co., research laboratories, Brooklyn 1, N. Y.

[3] Barrett Division, Allied Chemical & Dye Corp., research laboratories, Edgewater, N. J.

The careful and exhaustive extraction of rubber removed all but extremely minute traces of moisture and fat acid. The rubber was then compounded and cured for various lengths of time at 287° F. The physical and chemical properties of the resulting vulcanizates are listed in Table 1.

TABLE 1

EFFECT OF FATTY ACID ON DINITROBENZENE VULCANIZATION

	1	2	3	4	5
Extracted pale crepe	100.00	100.00	100.00	100.00	100.00
m-Dinitrobenzene	6.00	6.00	6.00	6.00	4.00
Litharge	9.00	9.00	9.00	9.00	5.34
Stearic acid	...	5.65	8.47	11.3	5.80

Physical Properties

Sample	Time at 287° F (min.)	Tensile strength in (lbs. per sq. in.)	Elongation (percentage)	M-300 (lbs. per sq. in.)	M-500 (lbs. per sq. in.)
1	15	1200	670	100	350
	20	1200	700	150	400
	30	1200	720	200	600
2	15	1300	740	125	300
	20	1800	720	150	400
	30	1200	610	200	500
	45	900	530	200	650
	60	900	540	225	800
3	15	1160	740	100	200
	20	1400	690	150	300
	30	1600	650	150	450
	45	2000	640	200	600
	60	1600	600	250	600
4	15	800	790	100	200
	20	800	710	150	300
	30	800	600	175	350
	45	1350	650	200	400
	60	1400	610	200	600
5	15	400	800	100	200
	20	500	730	100	200
	30	1200	750	100	250
	45	1250	770	150	300
	60	1200	700	175	400

Iodine number

Time of cure at 287° F	0	15	20	30	45	60
Extracted crepe	362	—	—	—	—	—
Sample 1	—	312	315	315	—	—
2	—	312	313	311	309	302
3	—	313	313	302	311	303
4	—	313	313	311	309	302
5	—	348	342	340	328	329

These data indicate that the amount or even the absence of fat acid (or potential water) does not appreciably affect the physical characteristics or the rate and extent of change in unsaturation. In sharp contrast, if the amounts of dinitrobenzene and litharge are reduced, there is a definite decrease in the number of double bonds consumed during the reaction and in the rate of vulcanization as measured by physical properties. In each case, unsaturation drops rapidly and quite sharply in the initial stages of the reaction. There is a small but definite further decrease in unsaturation over the normal curing

range. The magnitude of the original change in iodine number as well as the rate and extent of further changes in unsaturation in this region depend on the concentrations of litharge and dinitrobenzene employed.

Experimental Procedure.—The large-scale extractions were run in a two-liter glass Soxhlet extractor. About 100 grams of pale crepe was sheeted very thin and wrapped around wire. The wire was then rolled loosely and placed in the extractor. C. P. acetone (BP 58–59° C) was used as the solvent. The solvent was evaporated from a two-liter flask, condensed, and led into a vertical cylinder about 15 inches high, which contained the sample. When the liquid level in the cylinder reached the height of the side arm, the solvent and extract flowed into the two-liter flask. After one-day extraction the solvent in the cylinder was usually clear. At an appropriate time during the distillation on the first or second day the residual material in the two-liter flask was removed, fresh acetone added, and the extraction continued for 8–10 days. Following extraction the samples were immediately placed in a desiccator under carbon dioxide. Any remaining acetone was removed by using warm mill rolls when mixing the extracted samples to insure uniformity.

In general, A.S.T.M. compounding procedures were followed. The compounding ingredients were of high purity and of such a particle size as to permit passage through a 300-mesh screen. Before adding the reagents the mill rolls were warmed by hot water to 130°–140° F to bring about evaporation of any residual acetone in the rubber.

Unsaturation determinations were made essentially by the procedure of Blake and Bruce[3], which is a modification of that of Kemp[4].

PHYSICAL PROPERTIES OF NONSULFUR VULCANIZATES

It is impossible to gain a clear picture of the physical properties which can be obtained by the use of nonsulfur vulcanizing agents unless the conditions of vulcanization (including the use of modifying agents) are varied widely and are carefully specified for each experiment. This point is also true of sulfur vulcanization. The simple sulfur vulcanizates have physical characteristics inferior to those of a modern formulation, which may contain highly developed sulfur accelerators, activators, reënforcing pigments, and antioxidants. It would, therefore, be misleading to compare the properties of a simple nonsulfur vulcanizate, in which no modifying agent or a casually chosen agent is used, with those of a modern sulfur vulcanizate which has been developed after many years of painstaking research.

In general the nonsulfur vulcanizing agents impart a faster curing rate than does sulfur. The tensile strengths of most nonsulfur vulcanizates are slightly—sometimes appreciably—lower than those of sulfur vulcanizates. Nonsulfur vulcanizing agents, however, are known which may impart a tensile strength up to 15 times greater than that obtainable with sulfur, *e.g.*, the action of Durite S2666 in Hycar-OR nonblack stocks. In most cases, particularly with synthetic rubbers, the aging characteristics of nonsulfur vulcanizates are outstanding. A few of the simple nonsulfur agents, *e.g.*, benzoyl peroxide, impart poor aging characteristics, but this may be rectified by choice of a suitable antioxidant[5].

The characteristics of nonsulfur vulcanizates can best be judged individually. Many of these vulcanizates can be, and are worthy of being, developed to a much greater degree. In the sections that follow the physical properties of typical nonsulfur vulcanizates are shown. Data for the simple

vulcanizate are shown in each case. In addition to these, the effect of modifying agents is described whenever their action is known. Pertinent physical data from the literature are included wherever this action seems desirable.

Quinone Derivatives.—Benzoquinone itself is not a good vulcanizing agent, although its use has been patented[6]. Many quinone derivatives, such as chlorinated quinones and quinone oximes, however, are excellent vulcanizing agents for both natural and synthetic rubbers. Oxidizing agents are not strictly required for quinones. The use of oxidizing agents, however, always greatly improves the physical properties. If hydroquinones or other reduced forms are used, then an oxidizing agent is required. Some oxidizing agents are better than others for a specific vulcanizing agent, and Fisher has indicated this to some extent, particularly in his patents[7].

Table 2 shows results obtained with quinone derivatives in natural rubber. In Figure 1 are plotted the tensile strength *vs.* time of cure curves for two gum

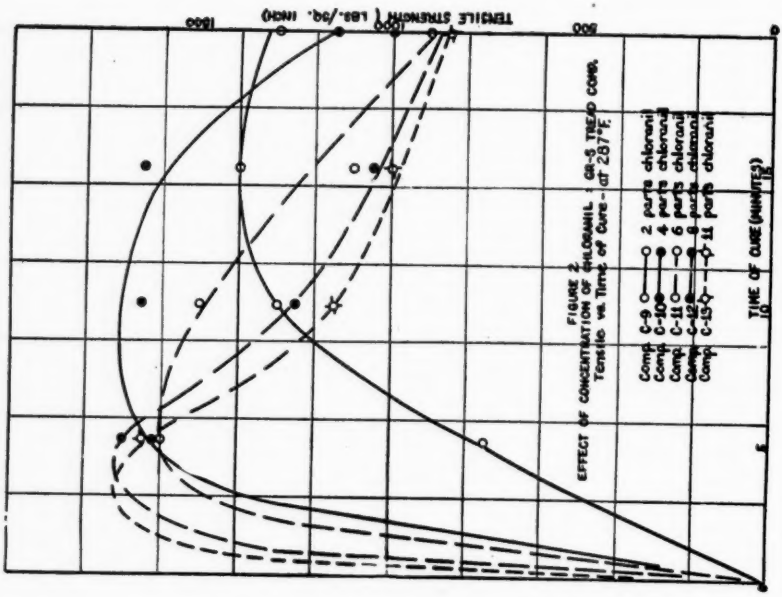
TABLE 2

QUINONE DERIVATIVES IN NATURAL RUBBER

Sample		Time at 287° F (min.)	Tensile strength (lbs. per sq. in.)	Elongation (percentage)	M-300 (lbs. per sq. in.)	M-500 (lbs. per sq. in.)	Shore hardness
C-1		15	20	300	—	—	17
Pale crepe	100	30	20	400	—	—	17
Quinone	10	60	20	500	—	—	17
Red lead	10	90	20	500	—	—	17
		120	20	500	—	—	17
C-2		15	200	820	—	—	23
Pale crepe	100	30	200	830	—	—	21
Chloranil	5	60	500	880	—	—	20
		90	540	870	—	—	20
		120	400	900	—	—	19
C-3		15	1185	550	210	900	—
Pale crepe	100	30	1320	500	300	1320	—
Chloranil	5	60	1000	480	310	—	—
Lead dioxide	10	90	1820	550	300	1110	—
		120	1380	490	300	—	—
C-5		5	1460	410	630	—	47
Pale crepe	100	10	2100	410	1100	—	53
Chloranil	5	15	1850	350	1430	—	56
Lead dioxide	10	20	2500	320	1800	—	56
Channel black (E.P.C.)	40	45	1900	300	1900	—	59
		90	1600	270	—	—	60
C-5a		15	810	250	—	—	50
Pale crepe	100	20	1690	350	1220	—	50
G M F (commercial *p*-quinone dioxime)	2	30	2280	420	1230	—	50
Red lead	20	45	1970	380	1300	—	50
Channel black (E.P.C.)	40	60	2390	410	1220	—	50
		90	2390	430	1220	—	50

stocks containing chloranil. The improvement effected by the use of oxidizing agents is clearly shown.

The action of chloranil on GR-S was also studied. Litharge and channel black were added in all cases, and the concentration of chloranil was varied. The results are shown in Table 3 and Figure 2.


TENSILE STRENGTH (LBS./SQ. INCH)
1500
1000
500
TIME OF CURE (MINUTES)
10
FIGURE 2
EFFECT OF CONCENTRATION OF CHLORANIL
Tensile vs. Time of Cure - at 287°F.
GR-S TREAD COMP.
Comp. C-9 — 2 parts chloranil
Comp. C-10 — 4 parts chloranil
Comp. C-11 — 6 parts chloranil
Comp. C-12 — 8 parts chloranil
Comp. C-13 — 11 parts chloranil

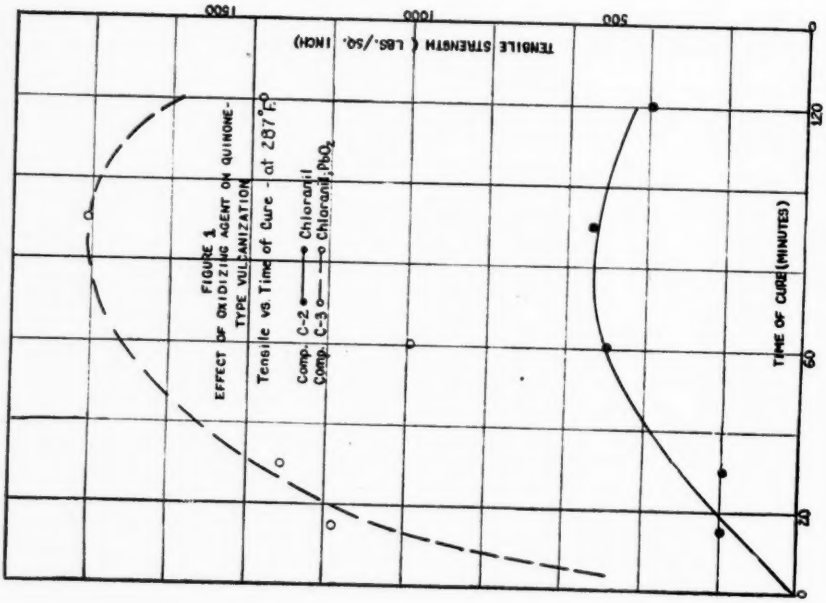

TENSILE STRENGTH (LBS./SQ. INCH)
1500
1000
500
TIME OF CURE (MINUTES)
120
60
20
FIGURE 1
EFFECT OF OXIDIZING AGENT ON QUINONE-TYPE VULCANIZATION
Tensile vs Time of Cure - at 287°F.
Comp. C-2 — Chloranil
Comp. C-3 — Chloranil, PbO2

TABLE 3

EFFECT OF CHLORANIL CONCENTRATION IN GR-S

Sample		Time at 287° F (min.)	Tensile strength (lbs. per sq. in.)	Elongation (percentage)	M-300 (lbs. per sq. in.)	M-500 (lbs. per sq. in.)	Shore hardness
C-9							
GR-S	100.0	5	750	770	100	300	43
Channel black (E.P.C.)	40.0	10	1300	750	200	500	47
Chloranil	2.0	15	1400	730	200	600	50
Litharge	10.0	20	1350	600	300	900	52
C-10							
GR-S	100.0	5	1625	6500	300	1000	50
Channel black (E.P.C.)	40.0	10	1650	500	600	1600	57
Chloranil	4.0	15	1650	470	700	—	57
Litharge	10.0	20	1150	330	850	—	60
C-11							
GR-S	100.0	5	1600	510	600	1450	53
Channel black (E.P.C.)	40.0	10	1500	390	900	—	60
Chloranil	6.0	15	1100	300	1100	—	62
Litharge	10.0	20	900	260	—	—	62
C-12							
GR-S	100.0	5	1700	540	650	—	56
Channel black (E.P.C.)	40.0	10	2150	340	—	—	60
Chloranil	8.0	15	1050	250	—	—	62
Litharge	10.0	20	1000	230	—	—	65
C-13							
GR-S	100.0	5	1650	460	—	—	58
Channel black (E.P.C.)	40.0	10	1150	250	—	—	62
Chloranil	11.0	15	1000	220	—	—	63
Litharge	10.0	20	850	230	—	—	63

TABLE 4

VULCANIZATION OF BUTYL RUBBER

Sample		Time at 307° F (min.)	Tensile strength (lbs. per sq. in.)	Elongation (percentage)	M-300 (lbs. per sq. in.)	M-500 (lbs. per sq. in.)	Shore hardness
GR-I	100.0						
Channel black (E.P.C.)	60.0						
Zinc oxide	5.0	15	no cure	—	—	—	—
Stearic acid	3.0	30	2460	860	240	—	—
Tetramethylthiuram disulfide	1.0	60	2520	780	440	—	—
Mercaptobenzothiazole	0.5						
Sulfur	2.0						
C-15							
GR-I	100.0	5	1900	650	600	1400	62
Channel black (E.P.C.)	60.0	10	1900	625	650	1500	62
Zinc oxide	5.0	15	1900	600	700	1650	63
Stearic acid	3.0	20	1900	580	750	1650	62
Red lead	10.0	30	1900	580	750	1650	63
G M F (commercial *p*-quinone dioxime)	2.0	40	1900	570	750	1650	63
C-16							
GR-I	100.0	10	1700	530	800	1600	73
Channel black (E.P.C.)	60.0	20	1600	500	800	1600	73
Zinc oxide	5.0	30	1600	500	800	1600	73
Stearic acid	3.0	40	1600	500	800	1600	73
Red lead	10.0	60	1600	510	750	1600	73
Dibenzo-G M F (commercial dibenzoate of *p*-quinone dioxime)	6.0	80	1550	530	750	1400	73

Some quinone derivatives are powerful vulcanizing agents and vulcanize natural rubber at room temperature. This activity may be utilized to particular advantage with some of the slow curing synthetics. Quinone derivatives are among the most practical of the nonsulfur agents, and current application is found in the vulcanization of Butyl rubber[8] in the manufacture of tire tubes. The following experiments (Table 4 and Figure 3) illustrate the rapid cures and high moduli obtainable with quinone derivatives in the case of Butyl rubber.

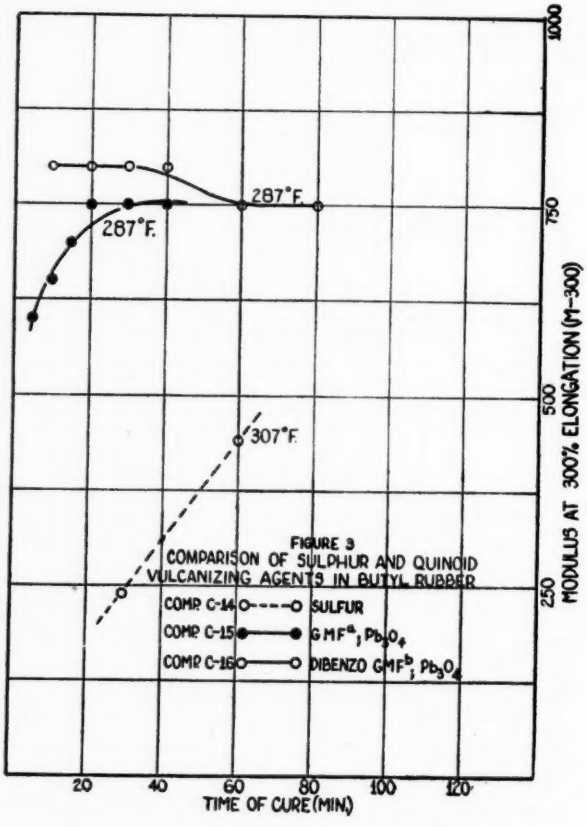


FIGURE 3
COMPARISON OF SULPHUR AND QUINOID VULCANIZING AGENTS IN BUTYL RUBBER

Nitrobenzenes.—Polynitrobenzenes impart properties to rubber that may be utilized commercially. The physical properties of the best nitrobenzene vulcanizates compare very favorably with the best obtainable by sulfur vulcanization of either natural rubber or GR-S[9].

The vulcanizing action of nitro compounds is directly related to the degree of nitration of the benzene nucleus. Trinitrobenzene is the most powerful of these reagents and is said[10] to be capable of vulcanizing rubber without the aid of oxidizing agents. Mononitrobenzene is a very weak vulcanizing agent. *m*-Dinitrobenzene is commonly used, as it appears to have the best general characteristics. In GR-S, *m*-dinitrobenzene has been reported to be an excellent vulcanizing agent, with particularly good aging characteristics. Litharge, which appears to be specific[9], is used as an oxidizing agent.

TABLE 5.

TYPICAL NITRO VULCANIZATES OF NATURAL RUBBER AND GR-S

Sample		Vulcanized at 307° F Time at 287° F (min.)	Vulcanized at 287° F Tensile strength (lbs. per sq. in.)	Elongation (percentage)	M-300 (lbs. per sq. in.)
LE-4[10]					
Pale crepe	100.0	25	3665	780	—
1,3,5,-trinitrobenzene	2.0	30	3520	760	—
Aniline	1.0	35	3450	760	—
Zinc oxide	150.0	40	3600	760	—
E-1					
Pale crepe	100.0	10	3140	530	1210
Channel black (E.P.C.)	40.0	15	3300	480	1600
m-Dinitrobenzene	5.0	30	2410	360	1910
Litharge	10.0	45	2100	300	2100
E-2					
GR-S	100.0	20	350	1220	—
Channel black (E.P.C.)	40.0	30	950	1050	200
m-Dinitrobenzene	3.0	45	1450	880	250
Litharge	5.0	60	2250	790	350
		90	2250	700	500
		150	2250	580	750

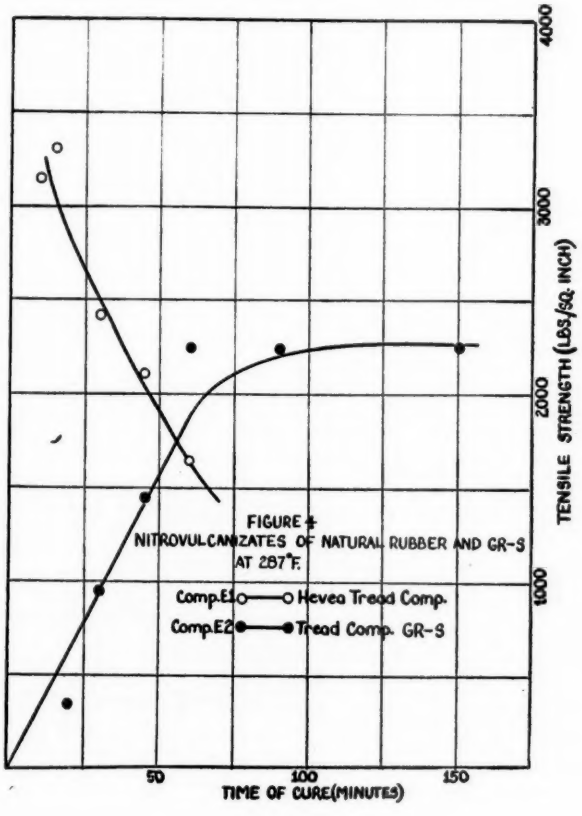


FIGURE 4
NITROVULCANIZATES OF NATURAL RUBBER AND GR-S AT 287°F.

Conflicting data in the early literature regarding the physical properties of nitro vulcanizates seems to be due to the use of excess quantities of the reagent or to unfortunate compounding practices[11]. Ostromislensky[10], in a detailed study of trinitrobenzene vulcanization, lists nine advantages of trinitrobenzene over sulfur as a vulcanizing agent. The use of certain aromatic amines (0.3-1.0 per cent) is recommended to protect the nitro vulcanizates from oxidation. Table 5 and Figure 4 show typical characteristics of trinitrobenzene and *m*-dinitrobenzene vulcanizates in both natural rubber and GR-S.

Benzoyl Peroxide.—Benzoyl peroxide does not appear to have potential application as a vulcanizing agent for rubbers, although its use has been advocated for rubberlike polyesters[12]. There are, nevertheless, definite procedures and techniques which improve peroxide vulcanization.

In mixing the batches care must be taken to keep the mill rolls cool to prevent thermal decomposition of the agent[5]. In some cases it may be necessary to sift the reagent before addition to the batch or otherwise insure proper particle size. Approximately 10 per cent of the peroxide appears to give best results. The compounds should be cured within a relatively short period after milling. If this is not done, a combination of autoöxidation and premature vulcanization often appears to take place. At 141° C the optimum cure is reached in a short time. Overcuring seems to have little effect on physical properties.

Unless other materials are used with benzoyl peroxide, the vulcanizates have poor heat resistance and aging properties. Mixtures containing sulfur (0.2–1.0 per cent) greatly improve aging[13]. Initial sulfur consumption is high, but is greatly retarded in a short time, probably owing to the formation of benzoic acid[5]. [It has been claimed that when sulfur and benzoyl peroxide are used together, vulcanization takes place exclusively by the peroxide[13]]. Perhaps the greatest improvement in agent is obtained by the use of certain of the usual antioxidants. The poor aging qualities of the simple vulcanizates, and the improvement imparted by antioxidants, are shown in Table 6[5].

TABLE 6

AGING PROPERTIES OF PEROXIDE VULCANIZATION[5]

	LA-6	LA-7
First latex pale crepe	100	100
Benzoyl peroxide	11.1	11.1
Age-Rite	..	1.0

Sample	Time at 147° F (min.)	Tensile strength (lbs. per sq. in.)	Elongation (percentage)	Shore hardness
LA-6	20	680	700	30
Aged 1 day 70° C	20	155	440	25
Aged 2 days 70° C	20	115	378	25
Aged 4 days 70° C	20	130	413	25
LA-7	20	600	840	30
Aged 1 day 70° C	20	640	850	30
Aged 3 days 70° C	20	510	785	29
Aged 7 days 70° C	20	525	795	28
Aged 14 days 70° C	20	430	761	25

The effect of a few of the sulfur accelerators has been investigated and they have been found to be ineffective or to act as retarders of peroxide vulcanization[5]. Metal oxides are not required[14], and their presence accelerates deterioration of the vulcanizate[13].

TABLE 7

EFFECT OF TEMPERATURE ON PEROXIDE VULCANIZATION[5]

Sample LA-5

(First latex crepe 100.0
Benzoyl peroxide 11.1)

Time min.	Tensile strength (lbs. per sq. in.)	Elongation (percentage)	M-700 (lbs. per sq. in.)	Shore hardness
		Vulcanization at 297° F		
10	615	740	470	38
20	730	750	500	39
30	715	760	450	40
60	640	740	500	41
120	715	760	450	41
		Vulcanization at 194° F		
30	200	1030	50	21
60	150	980	10	26
120	530	990	100	28
210	530	950	125	30

TABLE 8

PEROXIDE VULCANIZATION OF SYNTHETIC RUBBERS

Sample		Time at 287° F (min.)	Tensile strength (lbs. per sq. in.)	Elongation (percentage)	M-300 (lbs. per sq. in.)	Shore hardness
A-3		15	Stuck to mold	..	..	..
Buna-S	100.0	30	80	500	60	38
Channel black (E.P.C.)	40.0	60	90	470	60	38
Benzoyl peroxide	5.0	90	90	430	80	38
		120	110	450	90	38
A-4		15	900	480	600	68
Hycar OR-15	100.0	30	1050	400	650	68
Channel black (E.P.C.)	50.0	60	1400	420	1000	68
Benzoyl peroxide	5.0	90	1600	420	1100	68

TABLE 9

TYPICAL DIAZOAMINO VULCANIZATION PRODUCTS

Sample		Time at 287° F (min.)	Tensile strength (lbs. per sq. in.)	Elongation (percentage)	M-300 (lbs. per sq. in.)	M-500 (lbs. per sq. in.)	Shore hardness
B-1		15	1000	640	100	300	36
Extracted pale crepe	100.0	20	1000	640	100	300	37
Diazoaminobenzene	7.0	30	1100	620	100	300	37
B-2		30	590	580	—	400	30
Pale crepe	100.0	60	1320	720	—	310	30
Diazoaminobenzene	5.0	90	1210	710	—	380	29
Lead chromate	40.0	120	1200	680	—	380	29
B-3		15	800	420	500	—	48
GR-S	100.0	30	750	360	600	—	52
Channel black (E.P.C.)	40.0	60	1100	430	650	—	53
Diazoaminobenzene	4.0	90	1250	390	750	—	54
Lead chromate	40.0	120	1250	400	750	—	55

TABLE 10

PHENOLS AND AMINES AS VULCANIZING AGENTS

Sample		Time at 287° F (min.)	Tensile strength (lbs. per sq. in.)	Elongation (percentage)
LD-1[16]				
Natural rubber	100.0	30	110	1100
o-Aminophenol	10.0	90	190	830
Manganese dioxide	20.0	150	240	799
LD-2*				
Natural rubber	100.0	30	930	760
Manganese dioxide	30.0	90	930	570
Aniline	7.5	150	930	560
LD-3*				
Natural rubber	100.0			
Manganese dioxide	20.0	90	1020	800
p-Hydroxydiphenylamine	7.5	150	1825	710

Sample		Time at 287° F (min.)	Tensile strength (lbs. per sq. in.)	Elongation (percentage)	Shore hardness
D-1					
Pale crepe	100.0	15	20	800	10
Phenol	10.0	30	20	800	15
Red lead	10.0	60	20	800	18
		90	20	800	18
		120	20	800	18
D-2					
Pale crepe	100.0	2, 4, and 6½ hours at 287° F gave a definite cure,			
Aniline	10.0	but the samples were porous and somewhat tacky.			
Lead Dioxide	5.0				
D-3					
Pale crepe	100.0	20, 30, 240, and 390 minutes at 287° F gave a			
Phenol	10.0	definite cure, but the samples were porous and			
Lead dioxide	5.0	somewhat tacky.			
D-4					
Pale crepe	100.0	15	20	100	12
Diphenylamine	10.0	30	20	100	12
Red lead	20.0	60	20	100	15
		90	20	100	15
		120	20	100	15
D-5					
GR-S	100.0	15	60	300	33
Channel black (E.P.C.)	40.0	30	115	1000	46
Phenol	5.0	60	280	960	46
Red lead	20.0	90	290	850	48
		120	350	910	48
D-6					
GR-S	100.0	15	40	100	30
Channel black (E.P.C.)	40.0	30	40	100	32
Aniline	5.0	60	40	100	35
Red lead	20.0	90	40	100	35
		120	40	100	35
D-7					
GR-S	100.0	15	10	350	30
Channel black (E.P.C.)	40.0	30	10	350	32
Diphenylamine	10.0	60	20	450	33
Red lead	20.0	90	20	600	35
		120	20	600	37

All peroxide cures "bloom," *e.g.*, a substance (benzoic acid) crystallizes on the surface of the vulcanizate. The gum stocks are transparent. Vulcanizates are usually soft and occasionally somewhat porous.

Peroxide vulcanization may be used for synthetics as well as natural rubber, but in no cases are outstanding physical properties observed. Typical results are shown in Tables 7 and 8.

Diazoaminobenzenes.—Diazoamino compounds give vulcanizates that are clear and transparent and often age well[15]. 2,4,6,2′,4′,6′-hexachlorodiazo-

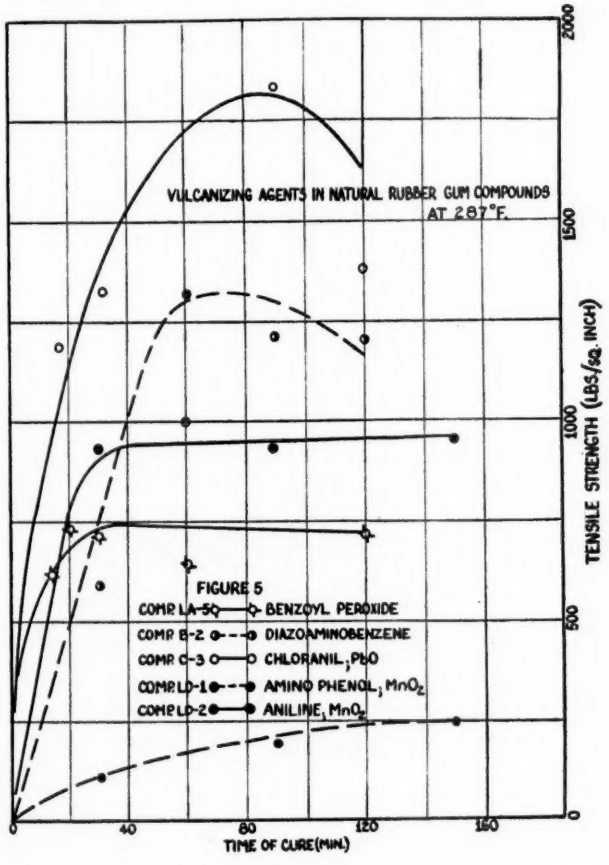


FIGURE 5

aminobenzene, for example, gives excellent products which are transparent, like molded pale crepe. *N*-benzyldiazoaminobenzene is said, not only to be an excellent vulcanizing agent, but to impart excellent aging characteristics as well. Fisher states that these agents do not require the presence of any other substance, but, as one of his patents[16] indicates, the properties of the vulcanizates are considerably improved by the use of an oxidizing agent[17].

Diazoamino compounds may be used to vulcanize both natural and synthetic rubbers, as shown in Table 9.

Amines and Phenols.—Amines and phenols do not seem to be among the practical nonsulfur vulcanizing agents. Tensile strengths obtained are gen-

erally low. An oxidizing agent is required in this type of vulcanization. Table 10 illustrates some of the properties of rubber and GR-S vulcanizates obtained with various amines and phenols. It is clear that these amines and phenols are not very effective vulcanizing agents.

Durite S-2666 (20).—One of the most interesting of all nonsulfur vulcanizing agents is Durite S-2666[19]. This material, a polymer of undisclosed composition[18], is an excellent vulcanizing agent for Hycar OS-20 and Hycar OR-15 (modified commercial copolymers of butadiene-styrene and acrylonitrile,

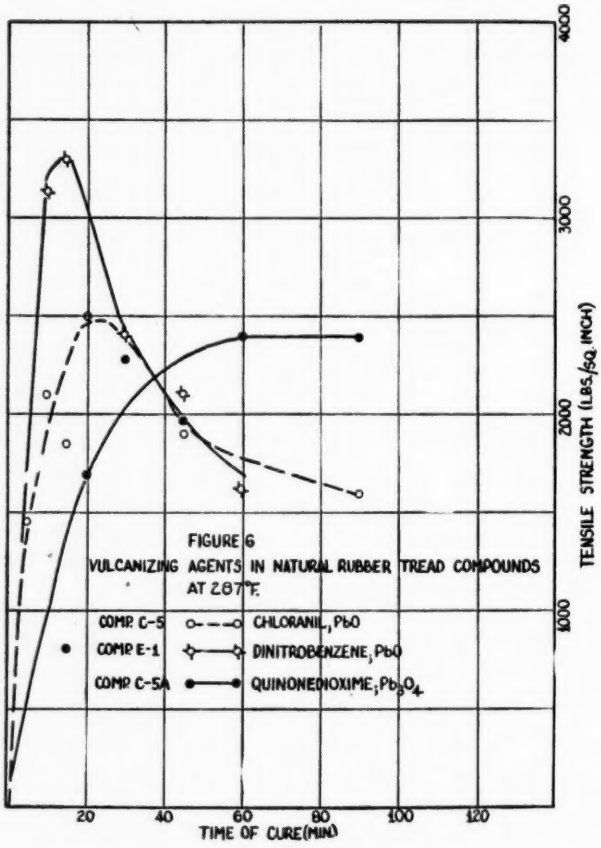


FIGURE 6
VULCANIZING AGENTS IN NATURAL RUBBER TREAD COMPOUNDS AT 287°F.

respectively). The physical characteristics of these vulcanizates are outstanding. Durite S-2666 imparts a tensile strength of up to 5000 lbs. per sq. in. to these copolymers, even in the absence of carbon black. Sulfur vulcanizates of corresponding (nonblack) composition have a tensile strength of about 300 lbs. per sq. in.

Since the composition of Durite S-2666 has not been disclosed, it is impossible to make a complete examination of its action during the vulcanization process. The supplier attributes the high tensile strength imparted by Durite S-2666 to the formation of long-chain cross-linkages between the rubber molecules. In such a case the long-chain cross-linkages would allow greater inter-

action of the intermolecular forces and a greater degree of orientation, which could result in greater strength.

Durite S-2666 does not require the presence of double bonds in the rubber to bring about vulcanization. It is capable of vulcanizing polyisobutylene, polyvinylacetate, and other materials. The presence of a simple double bond in a rubber, on the other hand, is insufficient to bring about vulcanization in the presence of the Durite agent. The Durite S-2666 does not vulcanize natural rubber, extracted natural rubber, or GR-S.

Summary of Physical Properties.—The wide variations in effectiveness of different nonsulfur-vulcanizing agents are brought out in Figures 5 to 7.

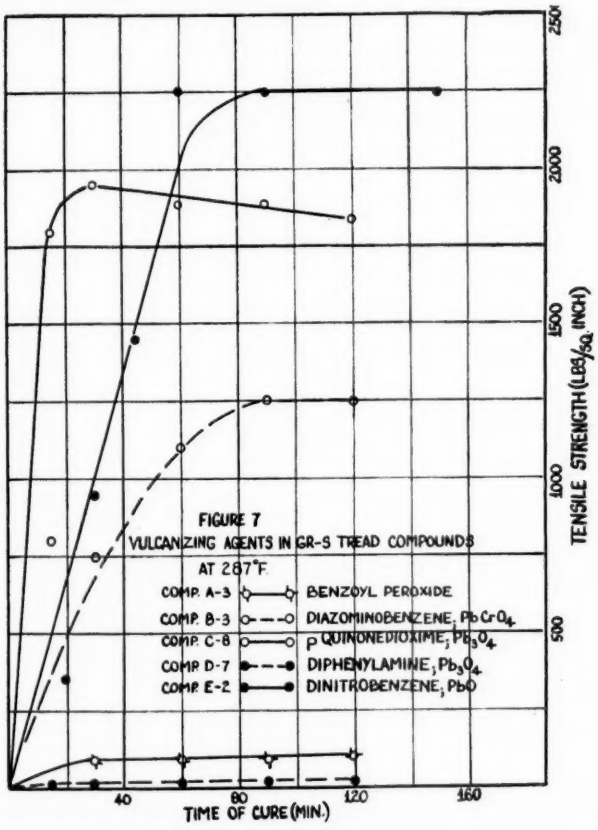


Figure 5 shows the tensile strength *vs.* time of cure for natural rubber gum stocks using different agents. Figure 6 shows a similar comparison for natural rubber tread compounds, and Figure 7 for GR-S tread compounds.

A number of these compounds have remarkably good properties as vulcanizing agents, particularly in view of the fact that optimum vulcanization conditions (temperatures, modifying agents, etc.) were almost certainly far from reached. The outstanding characteristics imparted by the new type of organic vulcanizing agent, Durite S-2666, is indicative of the possibilities that lie in this relatively unexplored field.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge and thank H. L. Fisher, G. S. Whitby, J. T. Blake, A. V. Tobolsky, C. K. Novotny, and E. A. Hauser for discussion and constructive criticism of the original manuscript.

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[16] Fisher, U. S. patent 2,170,191 (Aug. 1939).
[17] We are indebted to E. Krismann of E. I. duPont de Nemours & Co. for suggesting that, when the proper oxidizing agent is used, diazoaminobenzene vulcanization probably proceeds to a large extent through the mechanism suggested for the dinitroaryl compounds.
[18] Unfortunately this material is somewhat toxic.
[19] Durite Special Data, 1038 and 1039. Durite Plastics, Inc., **1943**.

ELECTRICALLY CONDUCTIVE RUBBER *

D. BULGIN

DUNLOP RUBBER CO., LTD., FORT DUNLOP, BIRMINGHAM, ENGLAND

GENERAL PROPERTIES OF CONDUCTIVE RUBBER MIXES

Introduction.—Electrically conductive rubber is the title given to the class of natural rubber and synthetic materials of which the electrical resistance has been substantially reduced from that of the pure polymer by the incorporation of suitable materials. Those almost universally used are selected from the groups of finely divided carbons of the type used for the reinforcement of rubber.

According to the type of the carbon and the amount which is incorporated in the polymer, the specific resistance in ohm centimeters of the resulting vulcanized compound can be between that of the pure polymer and something of the order of one ohm—a range 10^{15} to 1 ohm for natural rubber and GR-S. This resistance range covers all rubbers, insulating as well as conducting, and it is proposed to define conductive rubbers as those having a specific resistance of less than ten million ohms. Figure 1 shows the position of these conductive rubber materials compared with other well-known substances.

Even the most highly conducting rubber is a poor conductor compared with metals, and so the material is described more accurately as a semi-conductor.

The resistance range of 1 to 10^7 ohms is roughly from one thousand times more to one thousand times less conductive than tap water.

History.—The first conductive rubber recorded is the subject of a patent[1] for a graphite-rubber mixture, and in 1909, a patent[2] was granted for conductive ebonite for electrodeposition. The conductivity of these mixes was obtained by the incorporation of large amounts of graphite, gas carbon, retort carbon, and finely divided metals, and in general they would have poor mechanical properties compared with compounds used to-day.

In the period up to 1929 there was little further interest, apart from a British patent[3], in which it was proposed to use mixes containing graphite for electrical resistors and conductors, but between 1929 and 1932 several patents were issued for the use of conductive compositions containing graphite for elimination of corona discharge in electric cables.

A big advance was made when acetylene black was used in place of graphite and other coarse carbons. When this was first used is not recorded, but Heering[4] describes it for use in preventing corona discharge in high-voltage cables, and as the actual conductor in x-ray cables.

Habgood and Waring[5] have given a comprehensive review of the development of conductive rubber in the period 1929 to 1940, and their paper should be consulted for information on detailed developments.

In this country the Dunlop Rubber Co., Ltd., was producing conductive airplane tires in 1934, using Shawinigan (acetylene) black, and the Palmer Tyre

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 21, No. 3, pages 188–218, October 1945.

Co. also produced a conductive aero tire about this time, but the compositions used were not generally disclosed.

During 1938 the material jumped into some prominence in this country, and was exhibited at the Birmingham and Midland Institute in January[6] and was mentioned in papers by Rayner and Thornton[7] with regard to explosion risks in hospital operating theatres. The paper by Heering[4] on its use in high tension cables has already been noted.

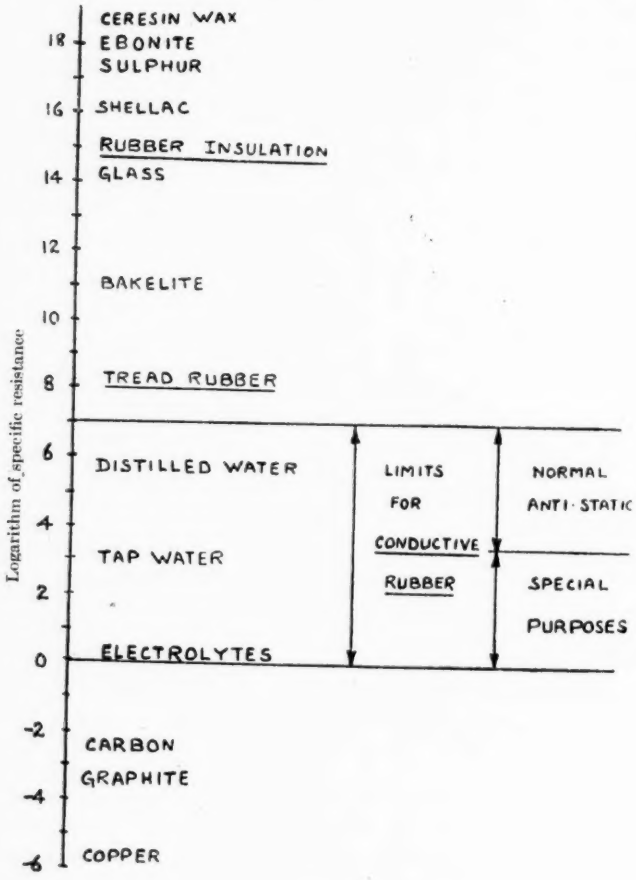


FIG. 1.

From 1938 to 1940 new types of carbon for conductive compounds prepared from natural gas were put on the market by American carbon black manufacturers under such trade names as W-9, Dixie-40, D-19, Graphon, etc., and this has continued with the manufacture of Statex-A, various grades of Spheron Black and other carbons sold specifically for their conductive properties.

These frequently permit the mechanical properties associated with the highest grade carbon black stocks to be attained, together with a good degree of conductivity, although frequently this is less than the maximum conductivity which can be obtained by using acetylene black.

The use of conductive rubber in various technical applications has been disclosed in the following patents.

Patent	Patentee	Use	Black Used
British 5757 (1882)	E. Trueman	—	Graphite
British 710 (1909)	Bourne	Electrodeposition on ebonite	Gas carbon, etc.
British 236,880 (1924)	Wade	Carrying currents	Graphite, carbon, metals in powder form
British 396,891 (1931)	N. Hollandske		
British 401,001 (1932)	Draaden		
British 404,519 (1932)	Kabel		
British 420,240 (1932)	Fabrik	Anticorona	
U. S. 2,074,826 (1932)	Boggs and Simplex Wire & Cable Co.	shields for	Graphite
U. S. 2,096,840 (1929)	E. Borman Siemens Schuckertwerke	cables	
British 455,193 (1935)	Borel	Electrolysis control on cable coverings	Gas carbon graphite, etc.
British 467,141 (1935)	Continental Gummiwerke A. G.	Conducting carding cloth	Graphite
British 490,546 (1937)	Harrison and Durham Cable Co.	Soil heating cables	Powdered carbon, graphite and metal
British 494,058 (1937)	Bulgin and Dunlop Rubber Co.	Fire-resistant articles	Acetylene
British 518,490 (1937)	Crawford and Goodrich Rubber Co.	Composite extensible sheet for deicing, etc.	Graphite
British 526,894 (1939)	Reynolds and Liverpool Electric Cable Co.	Compositions	Graphite, carbon and colloidal graphite
British 526,895 (1939)	Frost and Liverpool Electric Cable Co.	Cables	do.
British 527,634 (1939)	Emsley and Blackburn Aircraft Co.	Bonding cleats	Specified composition
British 527,734 (1939)	Morley and Scott and Standard Telephones	Cables	Acetylene
British 532,665 (1939)	Habgood and I.C.I., Ltd.	Conducting polythene	Acetylene, lamp, Kosmos T, F.4
British 534,818 (1939)	Thomas and Hutchinson Instrument Co.	Electrodeposition	Carbon and colloidal metals,
British 534,819 (1939)	do.	do.	do.
British 539,109 (1939)	Frost and Liverpool Electric Cable Co.	Cables	Acetylene
British 541,169 (1940)	U. S. Rubber Co.	Pile fabric floor covering	Acetylene (cement)
British 544,757 (1940)	U. S. Rubber Co.	Conductive tires	Acetylene (cement)
British 545,807 (1940)	Powell, Bulgin, Badham and Dunlop Rubber Co.	Tube vulcanization	Acetylene and others
British 555,070 (1942)	King, Bulgin and Dunlop Rubber Co.	Retarding	Acetylene and others
British 556,737 (1941)	U. S. Rubber Co.	Conductive tires	do.

From about 1937 onwards the use of acetylene and other blacks appears to have almost completely superseded graphite, metals and similar relatively coarse ingredients for making conductive rubber compositions.

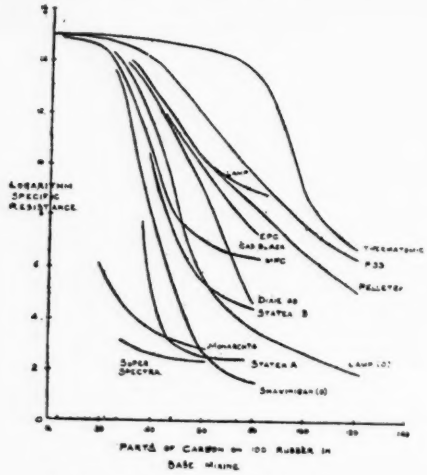


FIG. 2.—Logarithm of specific resistance of natural rubber compounds (o) = not remilled

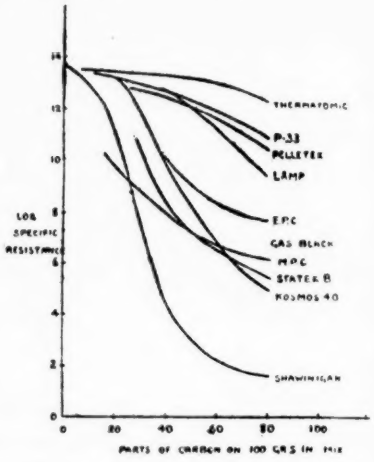


FIG. 3.—Logarithm of specific resistance of GR-S compounds (remilled)

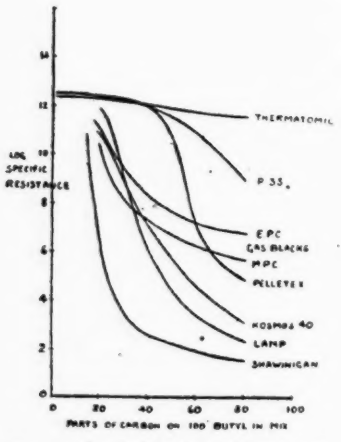


FIG. 4.—Logarithm of specific resistance of butyl compounds (remilled)

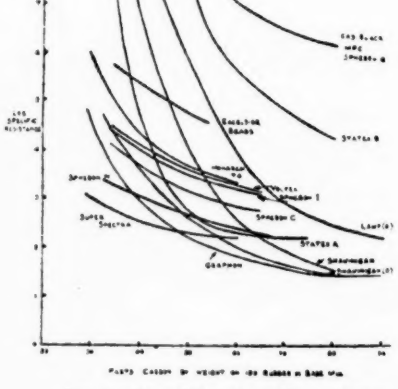


FIG. 5.—Logarithm of specific resistance of natural rubber compounds (o) = not remilled

Effect of amount of carbon.—In Figures 2, 3 and 4 are shown the logarithms of the specific resistance of vulcanized natural rubber, GR-S and Butyl (GR-I) compounded with various amounts of a number of carbon blacks of different types in the following base mixes.

BASE MIXES

Rubber	100	GR-S	100	Butyl	100
Sulfur	3.0	Sulfur	2.0	Sulfur	2.0
M.B.T.	0.85	M.B.T.	1.5	M.B.T.	0.5
Zinc oxide	5.0	D.P.G.	0.3	T.M.T.	1.0
Stearic acid	3.0	Zinc oxide	3.0	Zinc oxide	5.0
		Stearic acid	1.0	Stearic acid	1.0

The conductivity of the compositions varies both with the type and the amount of carbon present, increasing in all cases as the amount of carbon increases.

Table 1 tabulates the logarithm resistance values at 50 and 80 parts of carbon on 100 of the natural or synthetic rubber.

TABLE 1

Carbon	Particle Diameter A.U.	Rubber 50	Rubber 80	GR-S 50	GR-S 80	Butyl 50	Butyl 80
Thermatomic	2740	14.5	13.5	13.2	12.3	11.6	11.4
Lamp (O)	970	5.8	2.5	—	—	—	—
Lamp	970	11.5	9.0	12.0	9.5	4.3	2.3
P-33	910	11.5	9.8	12.2	11.0	11.3	9.0
Pelletex	820	11.1	8.5	12.2	10.5	10.4	4.8
Shawinigan (O)	430	2.6	1.5	—	—	—	—
Shawinigan	430	4.2	1.6	3.2	1.6	2.3	1.5
Dixie-40 Kosmos-40	470	10.8	4.8	8.4	5.0	5.5	3.1
Statex-B	360	7.5	4.7	7.3	5.3	—	—
Statex-A	340	2.9	2.2	—	—	—	—
Spheron-Gde 9 Spheron-EPC	300	11.2	7.6	9.2	7.5	7.5	6.7
Spheron Gde 6 Spheron-MPC	280	8.0	6.3	7.3	6.1	6.6	5.6
Spheron-N	—	2.7	—	3.3	—		
Spheron-C	—	3.2	—	3.5	—		
Spheron-I	—	3.5	—	3.4	—		
Excelsior Beads	—	4.8	—				
Voltex	—	3.6	—				
Monarch-74	—	3.7	—				
Super-Spectra	130	2.3	—				

(O) signifies stock not remilled after mixing.

If conductive rubber is defined as rubber with a log specific resistance of less than 7, the carbons of major interest are listed below. The log resistance/loading curves are drawn to a larger scale in Figure 5 for natural rubber stocks only.

Lamp black
Shawinigan black
Spheron Grade 6 and channel blacks of finer particle size
Dixie-40 (at high loadings)
Statex-B
Statex-A
Spheron-N
Spheron-C
Spheron-I
Excelsior Beads
Voltex
Kosmobile
Super-Spectra
Monarch-74
Continental R20, R30, R40

Effect of Type of Carbon.—It will be seen from the curves in Figure 5 that the carbons above are divisible at sight into groups which differ in that one group has a high initial resistance which falls rapidly to give low values of resistance, whereas the other group has a lower resistance at low loadings on the rubber, but a higher resistance at the higher loadings.

The division is:

Group I. Shawinigan, Lamp (and possibly Statex-A).
Group II. All channel blacks (Spherons 1 to 6, I, N, and C) Voltex, Kosmobile, Excelsior Beads, and color blacks (Super-Spectra and Monarch-74) and Statex-B.

This division is not absolute, furnace carbons have characteristics intermediate between these extremes.

Effect of Particle Diameter.—In Figure 6 it will be seen that there is not sustained relationship between the diameter of the carbon particle and the electrical resistance of the mix. However, for those carbons which are prepared by similar methods, for example, the group of blacks prepared by burning natural gas in proximity to steel surfaces, there is a systematic decrease in resistance with decrease in particle diameter. This conclusion is in general agreement with that of Cohan and Steinburg[8], who showed that the log resistance decreases linearly with particle diameter for carbons which have similar crystal structures.

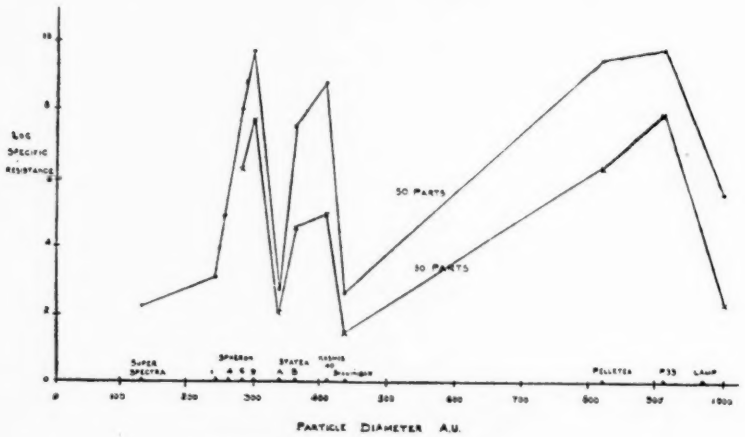


FIG. 6.—Resistance and particle diameter.

If, however, the volatile content or the crystal structure of the carbon particles change, as occurs when carbons are prepared by different methods, the effect of particle size on resistance is masked by other factors so that no general trend of the resistance in rubber from a knowledge of the particle diameter can be indicated except in the case of closely related carbons.

Relationship between resistance of the carbon in powder form and in the compound.—From the log resistance-carbon loading curves, Figures 2, 3, 4 and 5, it is possible to construct a graph of resistance against the fractional loading of black in the rubber. The relationship holds over a wide range of carbon loadings and can be expressed by the general equation:

$$R = e^{\left(\frac{a}{F}\right)^P}$$

where R is the resistance; a, P are constants; F is the fractional loading of carbon on the total mix; and e is the base of natural logarithms.

From these equations can be calculated the value of the resistance of "mixes" consisting of an infinite proportion of carbon to rubber, *i.e.*, of the carbon. The value obtained is of similar order to that determined by direct experimental determination on the carbon in compressed powder form. This correspondence of values, although of theoretical importance, is not of assistance in the evaluation of carbons in rubber without rubber tests being carried out, as the con-

stants, a and P in the above equation vary from one type of carbon to another, and so the resistance of a compound containing carbon can be calculated only if the values of a and P are known.

As the data in Table 2 show, there is, in effect, no direct relationship between the dry carbon resistance and the resistance of a rubber mix containing 60 parts of the same carbon.

TABLE 2

Black	Particle diam. (A.U.)	Log R at 60 parts loading in rubber	Specific resistance of powder under 680 lbs. per sq. in.	Log of ratio rubber/powder resistance
Thermatomic	2740	14.3	7.8	13.4
Lamp (O)	970	5.5	.86	5.6
P-33	910	12.0	9.6	11.0
Pelletex	820	10.5	1.05	10.5
Dixie-40	470	8.8	—	—
Shawinigan (O)	430	2.5	.47	2.84
Statex-B	360	5.4	1.25	5.3
Statex-A	340	2.3	.95	2.3
Spheron-9 (EPC)	300	10.0	43.0	8.4
Spheron-6 (MPC)	280	7.1	4.4	6.4
Spheron-4	270	5.5	5.5	4.7
Spheron-1	240	3.0	1.6	2.8
Excelsior Beads	—	4.4	1.95	4.1
Voltex	—	3.3	1.65	3.1
Spheron-N	—	2.4	1.25	2.3
Spheron-C	—	2.8	1.25	2.7
Super-Spectra	130	2.2	5.3	1.7

(O) signifies stock not remilled after mixing.

From the practical aspect, the electrical properties of a conductive compound cannot be assessed from a knowledge of the particle diameter or the dry resistivity of the carbon except in the special case of carbons prepared in similar manner and so possessing similar volatile contents and crystal structures.

The crystal structure of the carbon particle does influence conductivity, and is discussed later.

Effects of processing treatment on conductivity.—Conductivity in rubber has been shown so far to depend largely on the type and quantity of carbon in the compound. The general character of the phenomenon of conductivity is not greatly dependent on the type of polymer used, so it can be concluded that the carbon is the factor in the mix responsible for the conductivity.

For conduction to take place, it is necessary that the carbon particles shall be either in contact with each other or not more than a few Ångstrom units apart. As the arithmetical average distance between the carbon particles is several hundred A.U. it is concluded that the carbon particles flocculate to form a structure in the rubber so that each particle is in close proximity to other carbon particles and has not remained distributed in a statistical random manner[9], otherwise little or no conductivity would result[5].

Conductivity develops only when conducting chains of carbon particles exist between the electrodes through the material; that is, in distinction to the major mechanical properties of compounded rubber, conductivity is a result of special structural arrangement of the carbon particles in the whole sample. In consequence of this requirement it is not surprising that various factors such as the action of certain ingredients which weaken or enhance the amount of structure, or mechanical flexing or swelling by solvents, should alter the conductivity significantly.

The structure is not fully developed in mixes immediately after milling, but appears to be formed by Brownian movement of the carbon particles (or groups of particles) in the mix. This is shown (Figure 7) by the high resistance of newly milled unvulcanized mixes and the decrease in resistance which takes place on standing or on heating the unvulcanized compound.

Certain carbon blacks of Group 1, notably lamp and acetylene blacks, are of coarse particle size and yet form compounds of exceptional conductivity (see Figure 5 and Table 2). This probably arises from differences in the crystal structure of these carbons compared with those of Group 2. Rossman and Smith[10] suggest that acetylene black has free energy forces around the particles which aid the formation of structure. It is found that carbons of this group

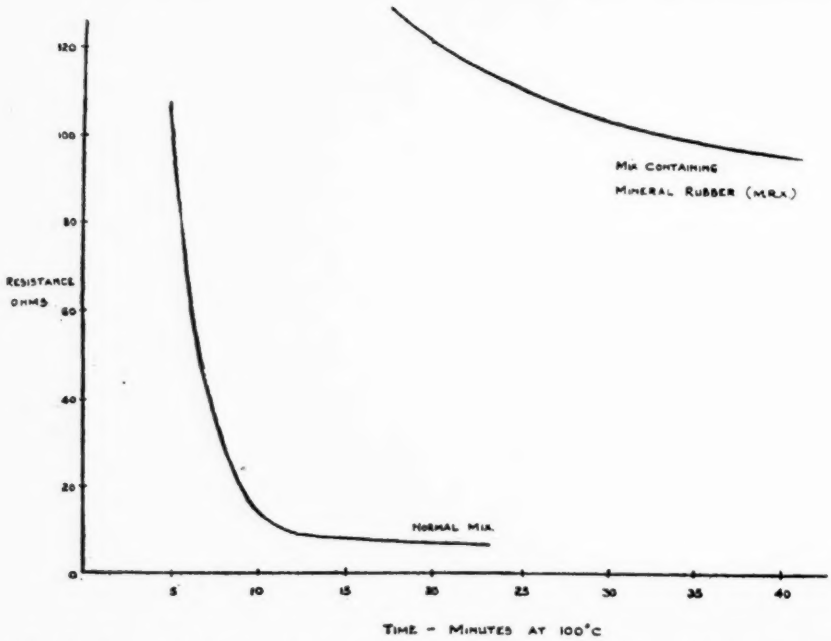


FIG. 7.—Change of resistance on heating unvulcanized mixes containing 50 parts of channel black

differ from those in Group 1 in that they rapidly increase in resistance if the stock is remilled (see Table 1), whereas blacks of Group 2 either improve or are substantially unaffected by moderate remilling. Figure 8 shows the effect of remilling lamp, Shawinigan and channel black stocks. The resistance increases continually in the first two cases, but decreases in the last case unless milling is carried out a large number of times. This probably arises from the continuation of the dispersal of channel black aggregates during the first few remillings, which liberates individual particles and so continues to build up structurally arranged black more rapidly than milling is breaking down the structure. However, when these structural units are fully formed, further remilling breaks them down and the resistance increases again.

In the case of the coarse size and structure-forming blacks, the full structure is built up at the first milling, and remilling merely breaks down the structure

and so increases the resistance. This increase in resistance on processing causes considerable uncertainty in final resistance of articles made from Group 1 carbons, due to variations arising from factory processing, and generally makes the selection of carbons from Group 2 desirable, even though the conductivity developed may be rather less than that of Group 1 blacks. Since the conductivity of Group 2 carbons improves with normal remilling, this choice is well suited to industrial techniques.

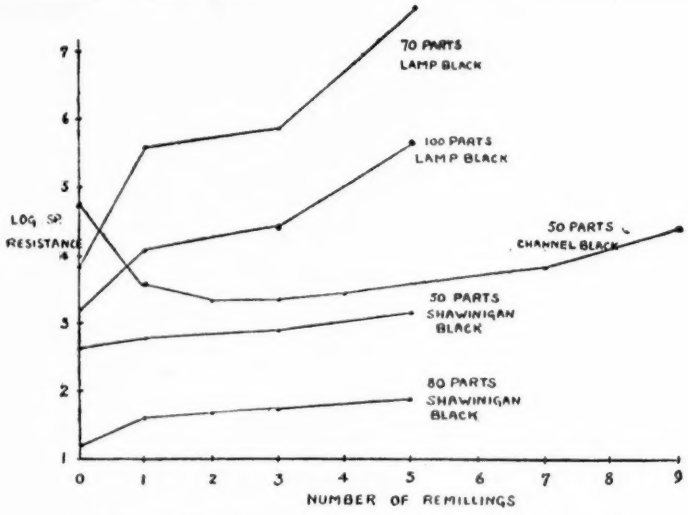


FIG. 8.—Effect of milling on resistance (parts black on 100 rubber)

Habgood and Waring[5] have shown that anisotropic conduction occurs with, and across, the direction in which the material is extruded. They showed that this effect gives rise to differences in conductivity by a factor as high as 30 to one when comparing conductivities along and across the direction of extrusion of acetylene black mixes.

By using mixtures of carbons (acetylene black plus fine particle-size gas blacks) they reduced the effect considerably, but indicate that the greatest reduction was brought about by the use of plastic rubber or peptizing agents in the rubber. The effect also occurs to a smaller degree with channel black types of conductive rubber, which, when processed in normal speed extruders, are found to have an anisotropy factor with and across the direction of extrusion or milling of between five and eight.

As electron-microscope photographs[11] have shown that there is no detectable anisotropy in the shape of particles, irrespective of their type or origin, it is possible that the anisotropy arises from the alignment during extrusion and milling of groups of carbon particles which have been formed during the earlier stages of preparation of the compound. If this is the explanation it indicates that the value of the interparticle forces after flocculation is sufficiently high to withstand the shearing forces occurring during milling and extrusion. The same conclusion has been reached by Wiegand[12].

Effect of the Polymer on Conductivity.—The type of polymer affects the precise value of conductivity obtained with a given loading of carbon, although the differences are not large, particularly at the higher loadings of carbon.

Compared with natural rubber, GR-S stocks have, in general, higher conductivities, but the difference decreases at high loadings. This result is in contradiction to that found by Cohan and Steinburg[8].

Butyl compounded with carbons has higher conductivity than either rubber or GR-S compounds.

Compared with natural rubber, GR-S stocks behave in general as if an extra 10 parts of black at any loading had been added, whereas for Butyl the effect is that of an additional 25 parts of black. These figures are given to illustrate the order of the change in resistance only, and not as any guide to compounding technique.

Comparative curves for Spheron-6 black and Shawinigan black in rubber, GR-S and Butyl are shown in Figure 9.

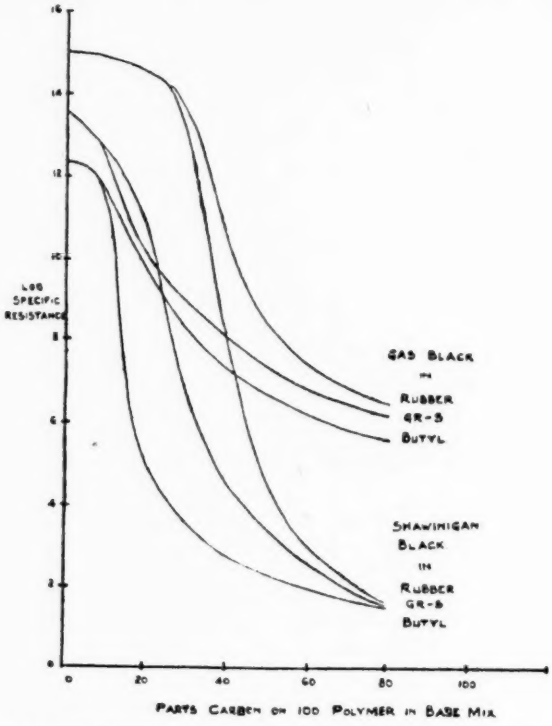


FIG. 9.—Resistance of gas black and Shawinigan black in rubber, GR-S, and Bu

TABLE 3

EFFECT OF VARIOUS POLYMERS ON RELATIVE RESISTANCE

Polymer	Black loading on 100 polymer 30	70
Rubber	1.0	1.0
Thiokol-FA	2.0	4.0
Hycar-OR	1.0	2.0
Perbunan	3.0	1.5
Neoprene-GN	1.0	6.0
Neoprene-I	8.0	20.0
GR-S	0.01	0.5

Table 3 gives the relative resistance for given loadings of channel black in polymers compared with those for rubber.

The divergencies are relatively small, but frequently the resistances at high loadings are not as low as those in rubber stocks, particularly in the case of the Neoprenes.

Effect of Compounding Ingredients.—In the case of natural rubber compounds, which have been more fully investigated than those of GR-S or Butyl, most compounding ingredients have little effect on conductivity with the exception of mineral rubber (M.R.X.), which considerably reduces the conductivity. This appears due to inhibition in the formation of black structure as is shown by the slow rate of decrease of resistance with time of heating in Figure 7. Final vulcanized compounds containing M.R.X. have many times the resistance of compounds not containing M.R.X. The reason for this phenomenon is not known; it may be due to preferential adsorption of M.R.X. on the surface of the carbon, or may be due to some effect of M.R.X. to increase the inner viscosity of the rubber (the viscosity associated with movement of the segments of the molecules).

The addition of softeners in general causes an increase in conductivity, which is probably due to reduction of the inner viscosity of the material as the effect of the melting point of the softener, *e.g.*, paraffin wax, can be detected in the vulcanized material.

The replacement of part of the polymers with powders generally results in an increase in conductivity.

The use of different accelerators does not cause much change; about five times change is the maximum that has been observed. This may be associated with the rate of scorching due to the accelerator, as suggested by Habgood and Waring[6].

Ebonite can be prepared with a considerable degree of conductivity as an increase in combined sulfur content appreciably increases the conductivity (Figure 10). This effect is more pronounced with gas blacks than with acetylene black.

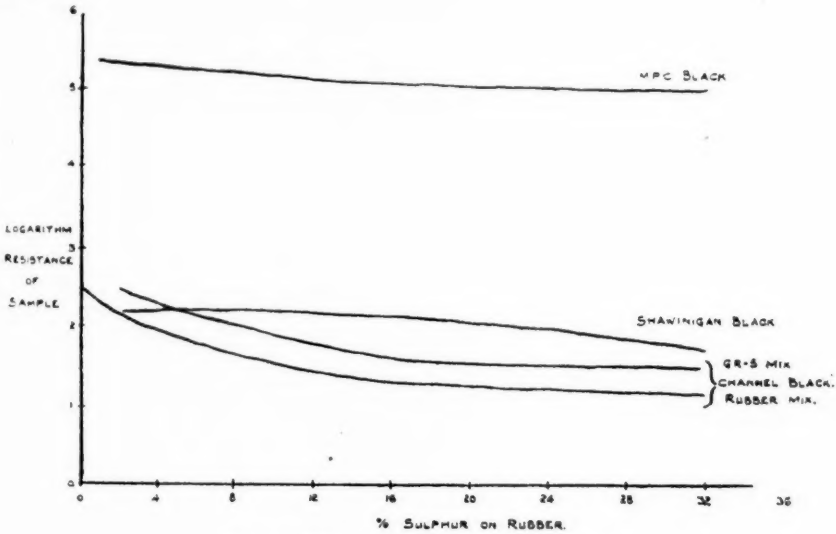


FIG. 10.—Effect of combined sulfur on resistance

Effect of Vulcanization.—The conductivity is substantially the same, irrespective of whether the material is vulcanized or unvulcanized, when due allowance is made for the effect of the combined sulfur and any metastable conductivity resulting from the temperature reached during hot vulcanization. This may be seen from the data in Table 4 on a 50 parts channel black

TABLE 4

Containing no sulfur	3.3
Cold vulcanization by Peachey process	3.4
Cold vulcanization by sulfur chloride	3.2
Hot vulcanized with 2.5 per cent sulfur	2.8

compound, each sample being heated to 120° C for 30 minutes and then cooled before measurement.

This indicates that conductivity is not a function of the vulcanization process.

Testing Procedure.—So far the important question of the effect of testing conditions on the conductivity values has not been mentioned.

Conductive rubber is in a class between insulators and metals, for both of which there are well established testing techniques. Skin effects, testing voltage, and time are factors which have to be taken into account when testing insulating materials, and these factors are of importance in conductive rubber. In addition, since it is flexible, it is subject to variation of conductivity owing to flexing and thermal history. These are problems which do not arise in the evaluation of the conductivity of rigid materials.

The definition of a test method is before a Sub-Committee of the British Standards Institution, so no attempt to recommend a method will be made. Experience gained over several years shows that the material exhibits a high skin resistance if the tests are made on an untreated surface, and that under this condition the result obtained is a function of both applied voltage and applied electrode pressure.

The magnitude of the effect is shown in Table 5.

TABLE 5

SAMPLES WITH UNTREATED RUBBER SURFACE

Example 1	2.1	5	110
	18.0	5	27
Example 2	19	5	368
	85	5	160
Example 3	1.5	0	250,000
		5	50,000
		50	2,000
		100	950
		300	450

Use of Aqua-Dag Electrodes.—Aqua-dag (colloidal graphite) electrodes painted on to the surface substantially eliminate the voltage sensitivity, but leave the material sensitive to applied pressure. Measurements made with this type of electrode are shown in Figure 11, and indicate that a minimum steady resistance can be obtained under applied pressures of up to 200 lbs. per sq. inch, depending on the hardness of the compound.

In the evaluation of the effective conductivity under service conditions, both the voltage and pressure used must be aligned with service conditions, a situation not always easy to achieve.

Moulded-in Metal Electrodes.—For laboratory and control purposes, an electrode system free from these effects is most desirable, and a satisfactory system has been found by moulding metal electrodes into the sample surface. These may either be brass-plated metal or consist of a sheet of thin tinfoil (0.001 inch thick) applied to the surface of the sample before vulcanization. This electrode system is free from voltage and pressure sensitivity.

Tests made with a potentiometric null method[13], in which, at balance, no current flows through the test electrodes and so eliminates any effects arising

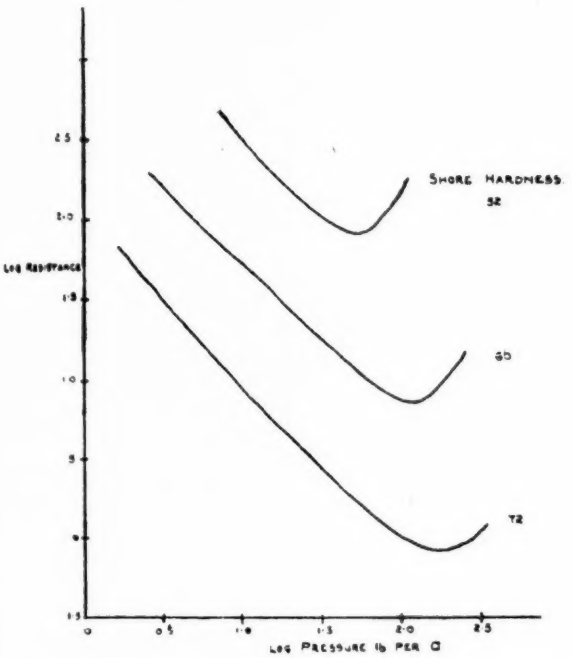


FIG. 11.—Effect of pressure on resistance with Aqua-Dag electrodes

from skin resistance, shows that there is no potential drop at either brass-plated or tinfoil electrodes. This indicates that the true bulk conductivity is measured with metal foil electrodes.

To avoid errors which may arise if the sample is flexed, it is desirable to use a sample so dimensioned that flexing does not occur accidentally; the majority of the measurements quoted in this paper were made at right angles to the direction of milling with tinfoil electrodes on the 2 in. × 2 in. faces of a 2 in. × 2 in. × 1 in. sample.

A systematic control of the temperature history of test-samples of conductive rubbers is desirable since the value of conductivity will be shown to vary greatly with thermal history.

FACTORS AFFECTING CONDUCTIVITY OF VULCANIZED RUBBER

Flexing.—It is assumed that conductivity arises from the carbon particles forming conductive paths in the material. Such a structure would be expected to be sensitive to flexing and elongation of the material, and this is found to be so.

On elongation the conductivity decreases to a few per cent only of the initial value (Figure 12). If the sample is held at this elongation the conduc-

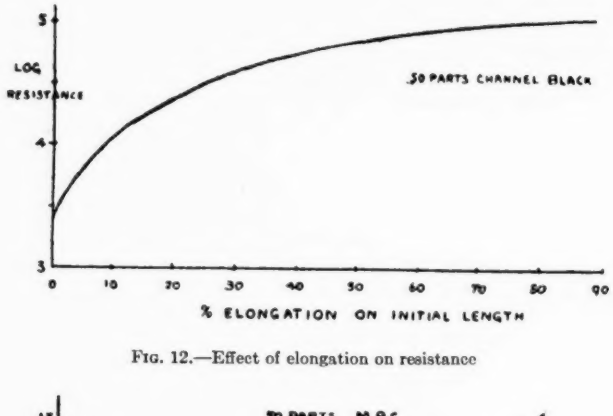


FIG. 12.—Effect of elongation on resistance

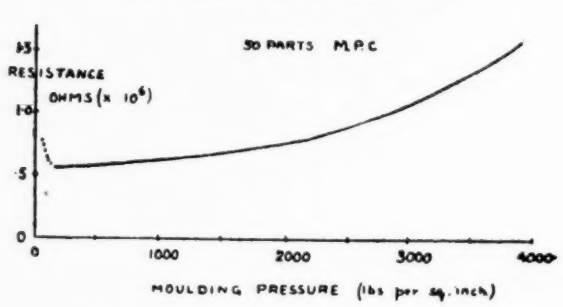


FIG. 13.—Effect of moulding pressure on resistance

tivity rises, and on release returns more or less quickly according to the temperature to its initial or stable value. The effect can appear considerably complicated by the previous thermal history of the sample. This point is of interest in the interpretation of the structural interrelationship of the carbon and the rubber, and is developed in a later section.

Moulding Conditions.—The temperature of vulcanization has a small effect which may be mainly associated with the temperature coefficient of resistance, but the pressure applied during moulding has a significant effect, the conductivity decreasing with increase in moulding pressure. This is shown in Figure 13. This effect is probably due to bulk compression of the rubber under pressure. The expansion which takes place on release of the pressure may be expected to cause a small separation of the carbon particles, which leads to a relatively large decrease in conductivity.

On the other hand, some small but positive pressure during vulcanization appears essential, as open-cured or lap-cured samples have a considerably lower conductivity than moulded samples of the same compound formula. The

extent to which this effect occurs cannot be generalized, as different carbons behave in different manners, those in Group 1 giving considerably lower conductivity than those in Group 2. Table 6 shows the type of variation caused by open and mould vulcanization of the same compound.

TABLE 6

Curing conditions	Resistance (ohms)			
	Two samples of channel blacks from Group 2		Shawinigan black Group 1	Lamp, channel and acetylene mixed blacks
Mould cure	120	280	400	75
Open-steam cure	500	4,800	5,000,000	5,200
Lapped cure	300	2,200	37,000	2,000

Swelling Agents.—Any agent which causes the rubber to swell appreciably destroys conductivity, but this returns to its normal value when the rubber is free from the swelling agent. Very small amounts of swelling appear to be sufficient in some cases to destroy conductivity, but there does not appear to be sufficient adsorption from the vapors of swelling agents to affect the conductivity of rubber and GR-S, so it can be used to convey anaesthetic vapors, or used in proximity to solvents. Other polymers are considerably more resistant to swelling agents and enable conductive solvent-resistant compounds to be made.

The degree of loss of conductivity for conductive polymers immersed in swelling agents is closely related to the degree of swelling of the polymer, and articles which are to function in the vicinity of swelling agents should be made from polymers which are oil and petrol resistant.

Table 7 gives the resistance to oils and gasolines in order of resistance to loss of conductivity.

TABLE 7

(1)	(2)	(3)	(4)
Hycar-OR Thiokol-AF	Perbunan Neoprene-I	Neoprene-GN	GR-S Rubber

Temperature Coefficient of Resistance.—Conductive rubber has, in general, a negative value of temperature coefficient of the order of 0.5 per cent decrease per ° C for material tested while maintained in a static, unflexed state.

If, however, the material is flexed during the temperature cycle the value of the temperature coefficient is considerably increased and becomes about 2.5 per cent decrease per ° C.

This apparently anomalous effect arises in the following manner. With stationary conditions the temperature coefficient is of the same order as that for carbon, and this may be ascribed mainly to the variation of the resistance of the carbon itself, since the particles are presumed in contact with each other and the rubber to have little or no influence.

When the rubber is flexed some of the contacts between the carbon particles are broken and are remade at a rate determined by the mobility of the carbon particles in the rubber, so in this case the kinetic properties of the rubber molecules, as well as the properties of the carbon, determine the conductivity, and the temperature coefficient is considerably larger.

This characteristic gives rise to an interesting thermal hysteresis effect which is shown in Figure 14.

If a sample is flexed and left in a stationary state it attains a steady value of resistance. If the temperature is then raised the resistance decreases about 2.5 per cent per ° C, with increase in temperature to a new and steady value at each temperature. If the temperature is now lowered and the rubber not flexed, it retains substantially the resistance attained at the highest temperature reached, due to the retention of the carbon structure, but on flexing the resistance increases immediately to a value appropriate to the lower temperature. The explanation of this point is developed further in the discussion section of the paper.

In effect, therefore, conductive rubber has two temperature coefficients, one of about 0.5 per cent decrease per ° C, when the material is in a stationary state, and one of about 2.5 per cent decrease per ° C when the rubber is flexed. It should be noted that this effect varies with the type of carbon used, and in practice may appear more complex, particularly if the material is in a state of strain.

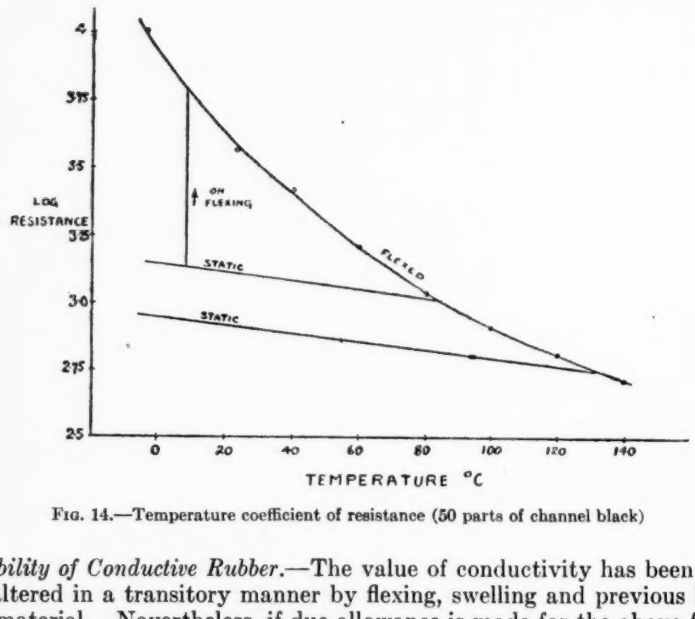


FIG. 14.—Temperature coefficient of resistance (50 parts of channel black)

Stability of Conductive Rubber.—The value of conductivity has been shown to be altered in a transitory manner by flexing, swelling and previous history of the material. Nevertheless, if due allowance is made for the above factors, conductive rubber possesses a stable conductivity, and even though severely aged and subject to considerable flexing, it does in most applications retain its conductivity at a sufficiently steady value to make it of use in many practical applications.

However, there may be a few exceptions to this generalization, and it is recommended that service tests should be made on new products, particularly as different types of carbon may give rise to different degrees of stability.

Practical Applications of Conductive Rubber.—Conductive rubber does not possess a steady definable resistance in the same sense as that of a metal, or nonflexible material, and hence, success in its application to practical problems requires careful consideration of the conditions of use.

The majority of problems in which it has been used, and to which it has given a satisfactory solution, do not demand an exact value of conductivity,

in fact it may be said that maintenance of a precise value of conductivity, and full use of its property of flexibility are, at present, incompatible demands. In a large number of applications conductive rubber is required only to conduct transitory currents, or to be maintained at a steady potential without substantial current flow. For this type of application full use can be made of the elastic properties of the material.

For other uses, in which conductive rubber is required to function as a resistance to dissipate electrical energy as heat, it is necessary to ensure that the rubber is not flexed to an appreciable extent; otherwise the variable resistance value which results causes corresponding variations in the heat dissipated, and these may be too large to be tolerated.

USES

Cables.—The use of conductive rubber to prevent voltage gradients sufficiently high to cause ionization of air in voids between the conductor and the insulation, and between the insulation and earthed coverings, was an early application, and was patented in 1929. A full description of cables working at 33 K.v., incorporating conductive rubber anticorona guards, as well as a 200 K.v. cable with the central core of conductive rubber as the element, used to carry the small currents required for x-ray purposes, have been described by Heering[4].

Conductive rubber has also been applied to the suppression of electromagnetic radiation, which causes interference with radio reception, by making the high tension leads from the ignition coil to the spark plugs on vehicles with a core of conductive rubber functioning as a resistance.

Static Dissipation.—The main field to which conductive rubber has been applied has been the dissipation of static charges in situations in which explosives, inflammable dust, or solvent vapors are present, or in solving other problems in which static charges give rise to undesirable effects or difficulties.

In connection with tires, conductive rubber has been applied as a complete tread and sidewall for tires for the earthing of static charges on aircraft, and for tires for buses and gasoline-carrying vehicles for elimination of static charges generated by friction. It has also been used on car tires for the same purpose, the static charge causing shocks and interference with radio reception; and for earthing of possible leakage currents on trolley buses by providing a low resistance path in parallel to the passenger. There have also been proposals to incorporate conductive rubber elements in and under the tread of tires for the purposes of static elimination instead of making the complete tire of conductive rubber.

In industrial problems, conductive rubber is used as rubber flooring to dissipate static charges in situations where there is a risk of explosions, as conductive soled shoes, and as containers, chutes and other mechanisms for handling explosive powders or materials. Belting is frequently a source of high static charges which have been the cause of explosions, and the facing of flat or V-belting with conductive rubber eliminates the charge without the use of conductive belt dressings.

It is also of use for conveyor belts handling papers, which tend to stick to nonconducting belts through static charges, and for conveyors for grain and other materials which readily acquire high and dangerous static voltages. Sandblasting has provided a further application, where its use as hose and nozzle removes the high static charges which are generated by the impact of the sand particles, and which can give severe shocks to the operator.

Other uses have been for spreading rollers, machine mountings and sponge rubbers, and the prevention of the generation of static charges which arise when walking on carpets. This is achieved by backing the carpet with conductive rubber and having a few conductive fibers in the pile of the carpet.

In hospital operating theatres, the warm low humidity conditions predispose to the generation of high static voltages which, in the presence of anaesthetic vapors and oxygen, gives rise to considerable risk of danger from fire or explosion originating from static charges on the rubber tubing, sheeting, flooring and other rubber articles inevitably present.

By making all rubber used in these situations of a conductive compound it is anticipated that this danger can be completely overcome.

Conductive Rubber as a Heating Element.—The remaining major application is the use of conductive rubber as a heating element. This involves, for successful use, a close control of the conductivity value, and the use of the material in an unflexed state. It is a minor, but important use, and it is claimed that it can be successfully applied to the deicing of propellors and aircraft wings, to heating gun mechanisms, and aviators' suits; and to assist the vulcanization of tubes and tires.

Dangers arising from Conductive Rubber.—The public are accustomed to regard any rubber, or article containing rubber, as a safe insulator for electrical purposes. The introduction of conductive rubber, with a conductivity many times greater than that of water, therefore introduces a considerable danger to the public from electric shock until, at least, they become as familiar with conductive rubber as with the insulating material.

To meet this danger the Home Office and the Factor Department of the Ministry of Labour and National Service strongly recommend that all articles made of conductive rubber shall be clearly and indelibly marked with a red label bearing the words "Electrically Conductive Rubber". This may either be moulded into the article, or firmly cemented to the material[14].

A second and separate risk arising from conductive rubber is the danger of ignition of the material, due to the passage through it of leakage current of sufficient intensity to cause heating and consequent ignition. This danger is aggravated by the fact that the temperature coefficient of resistance is negative, so that the resistance falls as the temperature rises.

The main danger arises if electrical faults develop to unearthed apparatus standing on a conductive rubber floor, so that the main voltage is applied through the rubber to the subfloor.

Fortunately, the purpose for which conductive rubber flooring is required is the dissipation of static charge, so relatively high specific resistances are quite adequate for this purpose, and a resistance value which dissipates the charge and yet does not pass sufficient current to cause overheating is possible.

The specific resistance of flooring for normal static conditions need not be less than 100,000 ohms, and this value is not likely to admit sufficient leakage current to cause overheating[15].

VIEWS ON THE MECHANISM OF CONDUCTIVITY IN RUBBER CONTAINING CARBON

The mechanism whereby electricity is conducted through rubber compounds containing carbon has been envisaged as due to the formation of chains, or filaments of carbon particles, which become continuous conducting paths from electrode to electrode. There is little doubt that this view is substantially accurate. A recent electron-microscope photograph (Figure 15) taken by

TABLE 8

Carbon (50 parts loading)	Particle diameter (A.U.)	Log R	B.S.I. Hardness
Lamp black	970	5.8	69
R-33	910	11.5	92
Shawinigan	430	2.6	50
Kosmos-40	470	10.8	70
Spheron Grade 6	280	8.0	58

Dr. Drummond on the instrument at Shirley Institute of a fragment of a normally prepared Shawinigan black compound shows clearly a coherent chain of carbon particles. Many electron-microscope photographs of carbon particles in air have shown evidence of strong flocculation, particularly in the case of lamp and Shawinigan blacks, and it is interesting to see that similar structure exists in a normally moulded rubber mix.

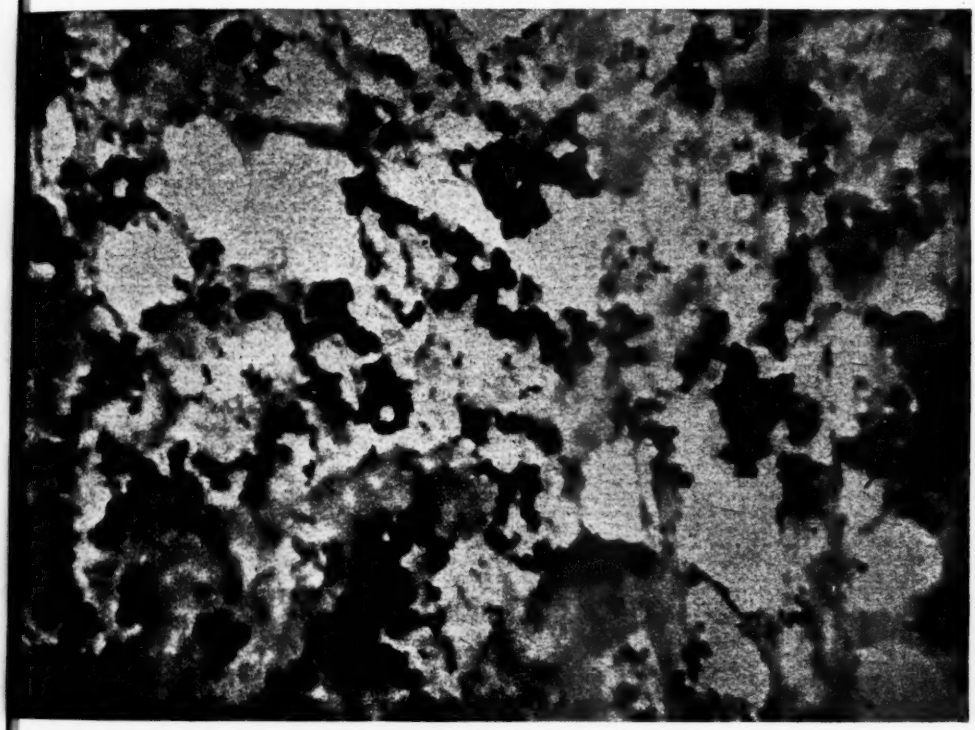


FIG. 15.

The forces on the carbon particles involved in flocculation arise from either Van der Waals or valence bonds of higher energy from the carbon atoms in the particles, but the magnitude of these forces is not identical for all types of carbon. For example, lamp black gives rise to much higher values of conductivity and hardness than does P-33 black, which is of almost identical particle size. The former may be presumed to give rise to a higher degree of flocculant

structure than the latter. Similarly, Shawinigan black gives much higher conductance and hardness than Kosmos-40 high-modulus furnace black, which is of comparable particle size.

Significance of the Crystal Structure of the Carbon Particle.—Cohan and Mackay[16] have examined the relationship between particle diameter, volatile matter and crystal structure of some channel blacks of different particle sizes, and conclude that, for carbons prepared by similar methods, which, therefore, may be presumed to have the same crystal structure and volatile matter, conductivity is determined by the particle diameter. After devolatilizing the same carbons by heating below 800° C, they showed that the adsorbed matter on the surface of the particles did not effect the conductivity to a major degree, and concluded that the most important factor determining the conductivity, apart from the particle diameter, was the crystal structure of the carbon particle.

An important step in the further elucidation of the question is due to Biscoe and Warren[17], who determined the structure of the crystal units comprising the particle by low-angle x-ray scattering. They showed that the carbon atoms are arranged in layers at graphitic spacing to each other, so forming a two-dimensional crystal plane. Three or four such layers are arranged parallel to each other to form the crystal unit, but the axes of the planes are not parallel to each other but at random angles. They coined the term "turbostratic" (unordered layers) to describe this arrangement of matter. The same structure has been shown to hold for coals and chars, and appears to be a fundamental unit in the formation of carbon units[18].

The carbon particle is formed by an assembly of a few thousands of these "turbostratic" units arranged at random.

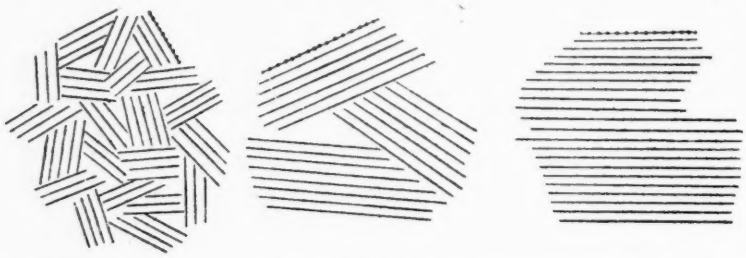
The dimensions in Table 9 are extracted from the paper by Biscoe and Warren[17].

TABLE 9

Black	Lc	La	a	c	Particle diameter
P-33	16.8	28.0	2.45	6.98	910
Shawinigan	26.6	47.5	2.42	6.86	430
Spheron Grade 6	12.7	20.0	2.45	6.82	280
Graphite	—	—	2.456	6.697	—

a = distance in A.U. between carbon atoms in plane of the layers.
c = distance in A.U. between carbon atoms at right angles to the layers.
La = dimensions of parallel layer group of combinations in plane of the layers.
Lc = dimension of parallel layer group perpendicular to the layers.

In Figure 16 (*a*) a schematic illustration of a portion of a Spheron-6 gas black particle is given. Each line represents a layer of carbon atoms in graphitic



(*a*) Portion of a gas black particle (*b*) Portion of a Shawinigan black particle (*c*) Graphite

FIG. 16.

arrangement, and each group of parallel lines a parallel layer group consisting of 3 to 4 graphite layers which comprise the unit, the dimensions of which are given in Table 9. Each layer consists of carbon atoms in graphitic arrangement of 2.456 A.U. (the a-axis) for all types of carbon, indicating that within the layer there is a true graphitic arrangement. However, the spacing between the layers (the "c" axis) is larger than in the case of crystalline graphite, indicating that the minimum energy arrangement has not been attained.

It will be seen by comparing Tables 8 and 9 that the larger unit size of Shawinigan black distinguishes it from Spheron-6 and P-33, and may be associated with its higher electrical conductivity.

Continuing this work, Rossman and Smith[10] determined the density of these same types of carbons in helium. From these determinations they deduced the average spaces between the randomly arranged parallel layer groups from which the particles are built, and found that in Spheron Grade 6 the mean spacing was 0.8 A.U., and the helium atoms could not enter between the crystal units. However, in the case of acetylene black, average spacing between the layers was considerably greater, about 6 A.U., and this enabled continued absorption of helium, due to diffusion of the atoms between the planes, to take place.

A particle of Shawinigan black (Figure 16 (*b*)) compared with a Spheron-6 particle thus consists of considerably larger units, with 6 to 7 layers of atoms, compared with 3 to 4 layers in Spheron-6. In addition, the Shawinigan units are assembled in a considerably less compact manner in the particle.

Rossman and Smith[10] conclude "that the loose association of the parallel layer groups in the particles of acetylene black may be reflected in residual forces at the surface of the particle. If these forces are sufficient to induce secondary association, or agglomeration between the particles, this may offer an explanation of the high electrical conductivity and other properties."

In Figure 16 portions of particles of Spheron-6 (*a*), acetylene black (*b*), and a graphite crystal (*c*) are shown. The whole particle of Spheron-6 contains about 3000 crystallites, whereas that of Shawinigan black contains about 1000 crystallites.

From the work of Biscoe and Warren[17] and of Rossman and Smith[10] it appears conclusive that free forces at the surface of the particles exist, due to the layers of atoms not being at minimum energy positions, and due to the differences in the degree of packing of the turbostratic units in the particles. This results in channel and Shawinigan blacks having different values of forces at the surfaces of the particles. These forces result in cohesion into the chains of particles necessary for electrical conductivity to take place, and high conductivity appears to be related to low values of B.S.I. hardness and other mechanical properties conferred on rubber by the incorporation of carbon.

In Table 10 (Figure 17) an endeavor has been made to correlate crystal structure with conductivity in rubber at loadings of carbon which give the

TABLE 10

Particle	Lc	La	Particle diameter (A.U.)	Black loading in 100 rubber (calculated to give equal spacings between surface of particles)	Log resistance	B.S.I. hardness
P-33	16.8	28.0	940	130	6.4	50
Shawinigan	26.6	47.5	430	60	2.8	41
Spheron Grade 6	12.7	20.0	280	40	9.0	65

same calculated* mean separation of the surfaces of the carbon particles and, although the data available are inadequate, the results suggest that both the resistance and hardness figures are considerably influenced by the crystallite size.

Influence of the Rubber on the Arrangements of the Carbon Particles.—In the preparation of rubber compounds, the carbon, which is in the form of aggregates of particles in air, is milled into the rubber and subject to shearing faces, so that individual carbon particles are detached from the aggregates and surrounded by rubber, whereby in a well milled stock a state of complete dispersion and wetting of each carbon particle by rubber is approached.

However, as the individual carbon particle or small aggregate of particles is reached, it is subject less to the shearing action of the bulk of the rubber, which acts through movement of whole molecules of rubber, and more to the kinetic motion of the chain segments comprising the rubber molecules. The

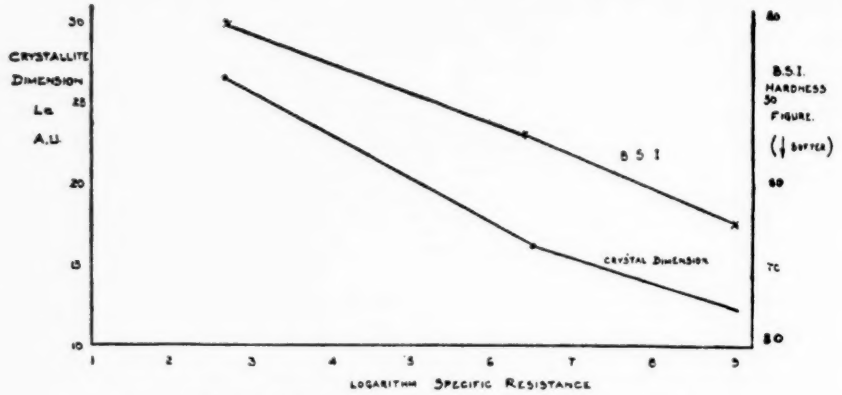


FIG. 17.—Crystallite dimensions and B.S.I. hardness—resistance at loadings resulting in equal average gaps between particles

kinetic motion of the segments of the rubber molecules cause the distributed carbon particles to be in Brownian movement and to drift from their mean positions, as a result of which contact occurs between the individual particles. As free forces exist at their surfaces they then coalesce to form flocculates, and ultimately complete chains and clusters of the carbon in rubber are formed.

These flocculates, in turn, are in Brownian movement and further coalescence takes place, but as the size of the unit increases its mobility decreases until ultimately it becomes relatively immobile. This is particularly the case if it is a large unit formed by the break up of the structure by the agency of externally applied forces.

Tuckett[19] and others have suggested that lack of agreement between dipole orientation time and Maxwellian relaxation properties of rubberlike polymers can be explained on the assumption that they possess two viscosities. The one is the viscosity of the whole molecules, and has a value around 10^7 poises for masticated rubber, and the second an inner viscosity appropriate to the individual segments of the rubber molecules.

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* $\text{gap} = r\left(\frac{4\pi d(112 + W)^{\frac{1}{3}}}{3W}\right) - 2$

Where r = particle radius A.U.; d = relative density; and W = parts of black in mix of 100 rubber + 12 nonrubber.

Deductions made by Carpenter[20] from gas solubility and diffusion, and by Amphlett[21] from the relaxation times of polar molecules in rubber, confirm this viewpoint, and give values between 10^{-1} and 10^{-2} poise for the inner viscosity, or one hundred millionth of the viscosity of bulk rubber for the movement of molecules in rubber.

However, gas black particles are many times larger than molecules, and so the effective value of resistance to their motion in the rubber may be assumed to be intermediate between the inner viscosity value of 10^{-2} poise and the macro-viscosity of 10^{7} poise.

Einstein's equation for the drift of particles in Brownian movement has been applied to the movement of particle aggregates of various sizes from 1 to 10^{7} particles in media of various viscosity values from 10^{-2} to 10^{7} poises for drifts of 100 A.U.

These are shown in Figure 18.

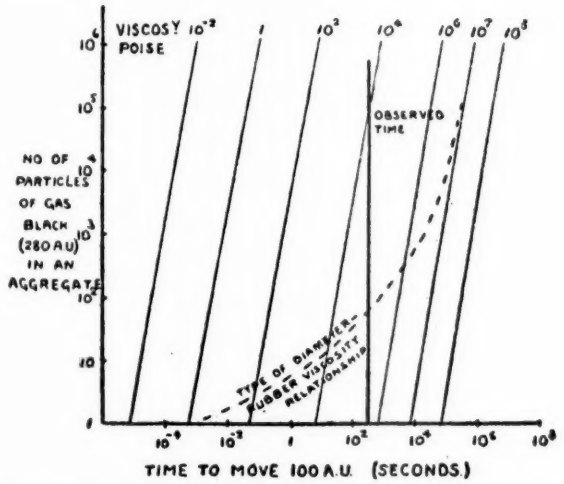
VISCOSITY POISE
OBSERVED TIME
NO OF PARTICLES OF GAS BLACK (280 AU) IN AN AGGREGATE
TYPE OF DIAMETER-RUBBER VISCOSITY RELATIONSHIP
TIME TO MOVE 100 A.U. (SECONDS)

FIG. 18.—Calculated time, motion, viscosity, and diameter relationship

Until data on the effective viscosity of rubber to particles of different diameter are obtained, the rate of flocculation of carbon black particles cannot be treated quantitatively, but the type of curve to be expected is shown in Figure 18.

By measuring the time required for the resistance of unvulcanized rubber to reach a substantially constant value of 100° C from Figure 7, or for vulcanized rubber from Figure 19 in which the time to reach 90 per cent, the ultimate value of resistance is plotted against temperature, a time of the order of 200 to 600 seconds is obtained.

This is the time required by a single particle in a medium with viscosity 10^{5} poises, or 10,000 particle aggregate in a 10^{4} poise medium, to move 100 A.U., and shows that the rubber must have an effective viscosity not greater than one-hundredth of that of the bulk material.

As the aggregates grow in size the rate of growth of structure slows down rapidly, due both to the growth in the size of the aggregate and to the increasing effective viscosity of the rubber. In effect structural growth takes place continually, but at an ever decreasing rate.

The substantial agreement for the time taken for structure build-up in both vulcanized and unvulcanized rubber indicates that the value of the inner viscosity is not substantially altered by vulcanization, although of course, vast changes are caused in the value of the macroviscosity.

Interparticle adhesion.—The energy actually released during flocculation according to calorimetric experiments is of the order of 0.2 cal. per cc., and it is evident that the basic mechanism of flocculation is the Brownian movement of the carbon particles due to the kinetic motion of the segments of the rubber molecular chain, and that the free forces of the particles only become effective when the particles are on the point of coalescence.

The energy liberation of 0.2 cal. per cc. of compound containing 10^{16} carbon particles indicates that the energy per particle is 2×10^{-17} cal., or roughly 10^{-9} erg. If a radius of action of 100 A.U. is assumed, this corresponds roughly to a mean force of 10^{-3} dyne per particle.

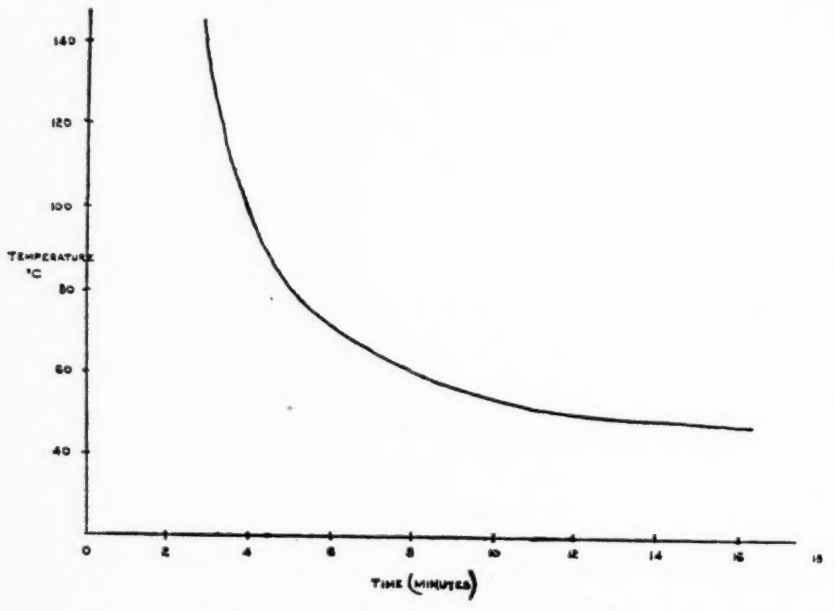

FIG. 19.—Time, at various temperatures, for resistance to reach 90% of ultimate value (50 parts channel black)

This value is of the order of 50 times greater than the accepted value of an interatomic bond, which averages about 2×10^{-5} dyne. This can be interpreted as meaning that Spheron-6 black particles exert a cohesive force equal to that of 50 atomic bonds. A similar order for the force has been obtained from the cohesive forces between carbon particles by consideration of tensile strength, tear resistance and energy loss by resilience measurements of carbon-rubber compounds in unpublished work. These measurements suggest that the adhesion between carbon particles is an important factor in the reinforcement of rubber by carbon.

How this force is related to the actual structure of the carbon particle cannot be stated in quantitative terms at the present time, but the looser structure

of acetylene black, with its higher value of free energy than the channel blacks, is reflected in the greater hardness and the lower pendulum resilience value of rubber stocks containing this carbon compared with comparable channel blacks[22].

As mentioned earlier, the electrical resistance of all black stocks is increased by remilling, and Table 11 shows that this increase is accompanied by increased

TABLE 11

Remilling (times)	0	1	3	5
Results on 100 parts lamp black in 100 rubber				
Log resistance	3.25	4.15	4.32	5.82
B.S.I. hardness	32	42	42	49
Pendulum Resilience (50° C)	0.719	0.736	0.749	0.741
Shawinigan black 60 parts on 100 rubber				
Log resistance	1.63	2.32	2.32	2.42
B.S.I. hardness	34	49	47	51
Pendulum resilience (50° C)	0.693	0.742	0.714	0.719

softness and increase in resilience of vulcanized lamp and Shawinigan black compounds. This would be expected if the number of black particle units cohering was reduced.

Structure in Rubber.—So far no consideration has been given to the actual value of conductivity obtained and the theoretical value which would be expected if all the carbon particles were in full contact with each other and formed complete chains, and if none were wasted by being in uncompleted chains or as isolated particles.

If it is assumed that all particles are in contact and that the effective resistance of the carbon is about 1 ohm, as determined by measurements on compressed carbons, then, in a 50-carbon-100-rubber mix, with about 28 per cent of the volume occupied by the carbon, the specific resistance between two electrodes with 100 per cent efficient conduction should be of the order of 4 ohms. Further, this value should be largely independent of the type of carbon used, and proportional to the carbon content of the mix, and it is clearly not in accordance with experimental facts..

It is feasible that conduction may take place through a relatively small number of continuous chains which would have to be of the order of 10^{-5} or less of the total possible number of chains at 28 per cent volume loading, and more or less at other loadings. In such a case the conduction would be according to the change of complete conductivity, paths being formed from the random arrangement of the carbon particles in the compound.

However, this problem is complicated by the fact that conduction can take place across gaps between conducting particles due to electron jumps[23].

Frenkel shows that the resistance of gaps between particles is related to that of resistance of the solid material by:

$$\frac{S_g}{S} = \frac{d}{l} e^{-kd}$$

where S_g is the conductivity of gap; S, the conductivity of solid material; d, the gap distance (cm.); l, the distance moved by free electrons ($\approx$100 A.U.); and k, the constant determined by work function of material (k for carbon = 1.8).

It therefore becomes practicable to calculate the value of the gap between particle surfaces required to give the observed conductivity.

The gap values required, calculated according to Frenkel's formula, are compared in Table 12 with those calculated by the mean arithmetic spacing in rubber.

The data in Table 12 show that considerably smaller gaps must exist than are calculated as the simple arithmetic mean if the conductivities calculated are to agree with those observed, the ratio of the gap, according to Frenkel's formula, being of the order 0.08 to 0.002 of the arithmetic mean gap.

TABLE 12

Carbon	Loading of carbon on 100 rubber	Log R	Mean arithmetic gap (A.U.)	Frenkel gap (A.U.)	Ratio Frenkel gap to mean gap	Ratio 50/80 ratios
Spheron-6	30	12.2	177	13.8	.078	1.0
	50	8.0	125	7.5	.060	
	80	6.3	90	5.1	.057	
Kosmos-40	50	10.8	190	11.8	.062	2.5
	80	4.8	135	3.5	.026	
Shawinigan	50	2.6	190	1.65	.0086	3.3
	80	1.6	135	0.35	.0026	
Lamp	50	5.8	440	5.3	.012	3.9
	80	2.6	320	1.0	.0031	
P-33	50	11.5	410	12.0	.029	.85
	80	9.8	290	9.8	.034	

With increase in carbon content from 50 to 80 parts on 100 rubber, the ratio of the Frenkel to the arithmetic gap is relatively constant for Spheron-6 gas black and P-33 black, but decreases by three to four times in the case of lamp and Shawinigan blacks. Presumably this is due to the higher free forces existing on the latter blacks arising from their different crystal structure, and indicates that as the gaps decrease they are further closed under the influence of the attractive forces between the particles.

This treatment does not decide whether conductivity takes place through a closed carbon chain structure, or whether a system with small gaps, less than 10 A.U. wide across which conduction takes place, exists in rubber. It does show, however, that a considerable closing-up of the particles into a structural system vastly different from mean arithmetic spacings takes place, and it is probable that the actual conduction is by a combination of both mechanisms, particularly at higher loadings of carbon.

Interpretation of the Phenomenon of two Temperature Coefficients.—In the section dealing with the properties of conductive rubber and in Figure 14 it was indicated that conductive rubber has two totally different temperature coefficients according to whether the rubber is held in a stationary state or is flexed during transition from one temperature to another.

The experimental observations are as follows. If a sample is reduced in temperature while held in the unflexed state its resistance remains fairly steady, but on flexing increases in resistance instantaneously to the appropriate value on the flexed state curve. If, however, it is flexed while the temperature is reduced, it reaches the same value by a steady path. The effect may be considered to correspond to a state in which a proportion of the carbon particles have been removed from sufficient proximity, or contact with each other to take part in the conduction process. When the temperature is raised, either with or without flexing, the apparent proportion of particles in the conducting state increases.

The maintenance of resistance value on decreasing the temperatures without flexing suggests that the cohesive forces between the particles are sufficient to maintain the particles in close proximity so that the resistance remains at its minimum value. This, however, is a metastable condition, for on flexing the resistance changes to a higher and stable value. This phenomenon may be qualitatively compared to supercooling.

The fall in resistance during increase in temperature can be explained as follows. It has been suggested that Brownian movement of the carbon particles is the mechanization whereby the carbon particles are caused to flocculate, and as the kinetic energy of a particle in Brownian movement is the same as kinetic energy of the molecules of the system in which it moves, it is of interest to relate this phenomenon to the well-established theory that the elastic properties of rubber arise from the kinetic motion of the segments of the rubber molecules[24].

If the data in Figure 14 are replotted in terms of the concentration of carbon which would be required to give the observed resistance, from data on log resistance-carbon loading curves, a graph can be constructed of the apparent carbon content.

This, when plotted against the absolute temperature in Figure 20, is a

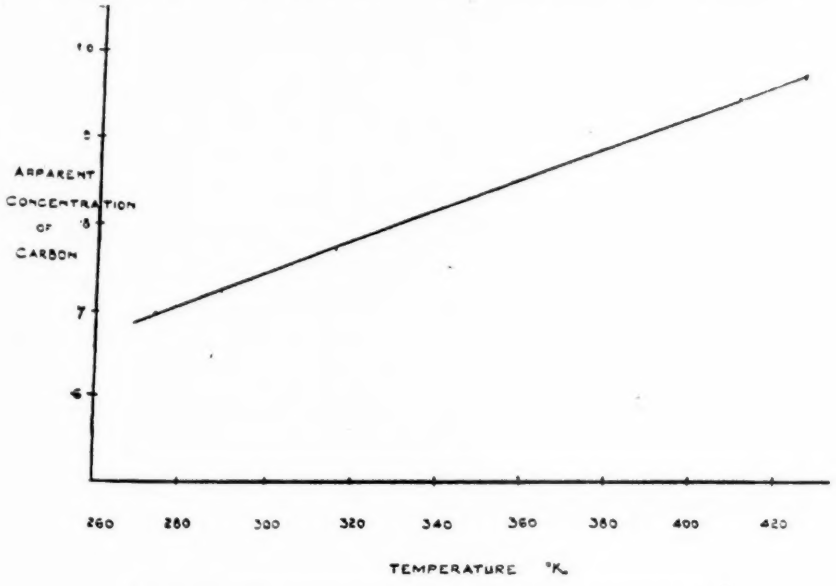

FIG. 20.—Relation of apparent carbon content and absolute temperature

linear function having the relationship, apparent carbon content = 0.0041 Temp. ° K.

This change in the apparent carbon content of 0.0041 per ° K is almost identical with the value of the gas coefficient of 0.0037 per ° K from the kinetic theory of gases.

The change in apparent carbon content at any temperature can be expressed as:

$$C_A = C_B(1 + a(A - B))$$

where C_A is the apparent carbon content at temperature A; C_B at temperature B; A and B are the temperatures ° K; and a is the temperature coefficient ($=0.0041$).

For ideal gases a similar equation can be written. The parallel nature of these equations, and similarity of the coefficients indicate that the amount of carbon taking part in the conduction process is proportional to the kinetic energy of the system.

It appears that a number of carbon particles proportional to the kinetic energy of the system at any given temperature become associated and so give rise to the appropriate value of conductivity. However, on decrease of temperature the cohesive forces between the particles maintain the structure set up at the higher temperature, although the kinetic energy of the system has decreased and corresponds to a lower number of particle cohesions. This is a metastable condition and reverts to the stable condition if the cohesion between the particles is overcome by externally applied stress.

This interpretation of the temperature coefficients on the basis of kinetic energy is in line with the view that the Brownian motion is the cause of flocculation in unvulcanized and vulcanized rubber.

CONCLUSIONS

Carbon particles in rubber are at first distributed as individual particles by the shearing action of milling, but the individual particles are in a state of Brownian movement due to the kinetic energy of the system. This causes the particles to drift about at a rate determined by the size of the particles, or particle aggregates, and the effective viscosity of the segments of the rubber molecules which is less than one hundredth of that of bulk rubber.

The particles thus soon come into contact with each other, and since they are of a disordered crystalline structure and possess relatively high free surface forces, they cohere.

The mobility of the aggregates of the particles is much less than that of the individual particles, due to their large size and size relative to that of the rubber molecules, so finally they are relatively immobilized into a scaffoldlike structure of carbon particles. This structure can be broken by external forces, and the broken structural units reform in vulcanized rubber to a structural state at a rate, and to an extent determined by the kinetic energy of the system.

The idea of increasing structure formation with rise in temperature is apparently contrary to the kinetic theory, but the persistance of a stable conductivity value in passage from a high to a lower temperature rules out particle motion as the prime cause of conductivity. Furthermore the attainment of a discrete value for the conductivity (Figure 19) at any temperature rather than an alteration of the rate of change towards some maximum value, suggests that temperature activated energy barriers exist—possibly between the carbon and the rubber—which have to be broken before the carbon particles are free to move.

Such a system explains the conductive properties of carbon-rubber mixes containing carbon particles of 250 to 300 A.U. diameter, but the properties of systems containing carbons of greatly different particle size may be considerably different.

There is some evidence that the cohesion of carbon particles into structural units is sufficiently high to withstand the shearing forces involved during milling and processing treatments of unvulcanized rubber, and so carbon structure

formation from individual particles is of an irreversible nature. As the structural units grow in size under the influence of the kinetic energy of the system they become increasingly less mobile. This gives rise to permanent reduction in conductivity if the structure built up is violently disturbed; for example, if unvulcanized rubber is remilled after appreciable structural formation has taken place.

ACKNOWLEDGMENTS

The author wishes to acknowledge the assistance of A. Crothers and J. Thomas of the Dunlop Laboratories in the measurements and the preparation of considerable numbers of samples, and to Parkinson and E. F. Powell for many helpful discussions, and to Amphlett and Carpenter for data on the reduced viscosity of rubber to molecules. The author is indebted to Drummond, of the Shirley Institute, for the electron microscope photograph reproduced in this paper, and to the Directors of the Dunlop Rubber Co., Ltd., for permission to publish this paper, which is based on work carried out in their laboratories.

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OXIDATION OF GR-S VULCANIZATES *

J. Reid Shelton and Hugh Winn

Case School of Applied Science, Cleveland, Ohio

GR-S vulcanizates are, in general resistant to aging at ordinary temperatures, but at elevated temperatures they undergo rapid changes resulting in increased modulus, decreased elongation, and poor flex-cracking resistance[1]. This general hardening at temperatures comparable to those encountered in service seriously impairs the usefulness of GR-S for certain purposes—for example, in heavy-duty tires. It is now generally accepted that the changes which occur in natural rubber during aging are primarily the result of oxygen attack, although the question was debated for many years and was the subject of numerous papers, which have been reviewed elsewhere[2]. It was to be expected, therefore, that the aging of GR-S likewise would involve reaction with oxygen.

The authors[3] previously demonstrated that more than half of the hardening of GR-S vulcanizates (as measured by the increase in modulus obtained after 5 days in air at 100° C) is caused by oxygen, since a much smaller increase was observed in a nitrogen atmosphere. Oxygen was also shown to be one of the factors involved in the flex-cracking of GR-S[4]. The present investigation was undertaken to study the mechanism of the oxidation of GR-S and the factors which influence the reaction. It was felt that the best approach to the problem was to determine quantitatively the rate at which oxygen combined with the vulcanizate.

The methods employed in analogous studies with natural rubber fall into three general types—gravimetric, manometric, and volumetric. The latter method, which follows oxygen absorption by volume change at constant temperature and pressure, was selected for this study because it is apparently more sensitive to small amounts of absorption than the gravimetric method, and the results are more readily interpreted than with the manometric method which involves a simultaneous change in volume and pressure. Dufraisse[2] preferred the manometric method for routine comparisons of oxidizability in a practical study of rubber; however, he also pointed out that the volumetric method is more convenient for studying the kinetics of the oxidation reaction, and that the data are more reliable. The manometric method does offer certain advantages of simplicity and ease of operation, but the volumetric method is best suited for studies of the type reported in this paper.

OXYGEN ABSORPTION MEASUREMENTS

The equipment is similar to that used by Kohman[5] in experiments with rubber. The assembled apparatus (Figure 1) consists of eight independent absorption units, each with its own sample tube, gas buret, and leveling bulb. Figure 2 is a picture of the sample tube, showing the mercury seal for the large

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 38, No. 1, pages 71–76, January 1946.

ground-glass joint and the hooks for suspending the samples at a point well below the level of the liquid in the constant-temperature bath. Capillary tubing connects the sample tube to its water-jacketed gas buret through a three-way stopcock, which also joins it to a manifold for evacuation and introduction of oxygen.

For the study of GR-S vulcanizates as reported here, the following procedure was employed: The assembled absorption bulbs (containing the appropriate weight of sample suspended from the hooks and a small lump of calcium oxide to absorb water vapor and carbon dioxide) are placed in the constant-tempera-

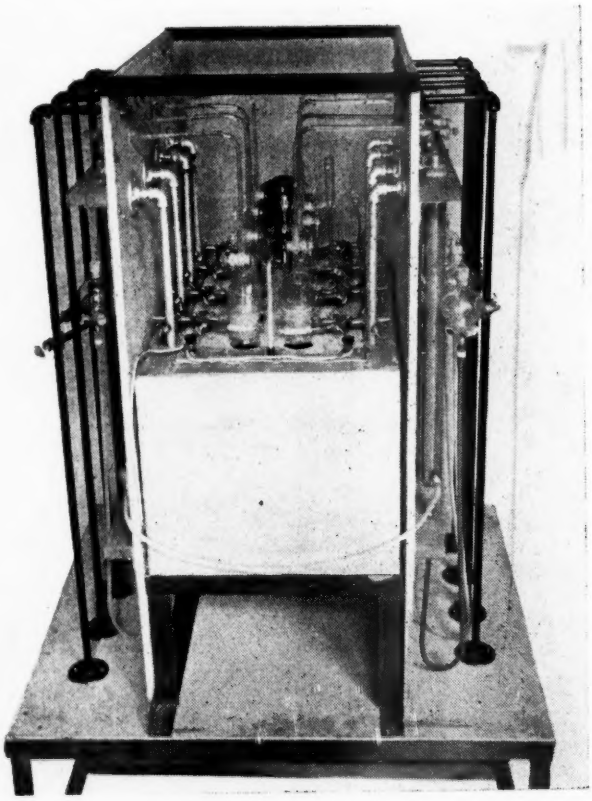

FIG. 1.—Absorption Apparatus

ture bath and connected to the gas burets. All tubes are then evacuated simultaneously through the manifold to remove the air from the system and as much as possible of the dissolved and adsorbed gases from the samples. Oxygen is then admitted, and the alternate evacuation and admission of oxygen repeated three times. The three-way stopcocks at the top of each buret are then turned so as to disconnect the manifold while allowing the absorption tube and gas buret of each independent unit to remain connected. The leveling bulbs are set to give the proper differential of mercury so that the total pressure in each tube is 760 mm. The initial volume is read and recorded, together with

the barometric pressure and jacket temperatures. Periodically the leveling bulbs are adjusted to maintain the desired pressure. This need not be exact, for experience has shown that small variations of pressure have only a negligible

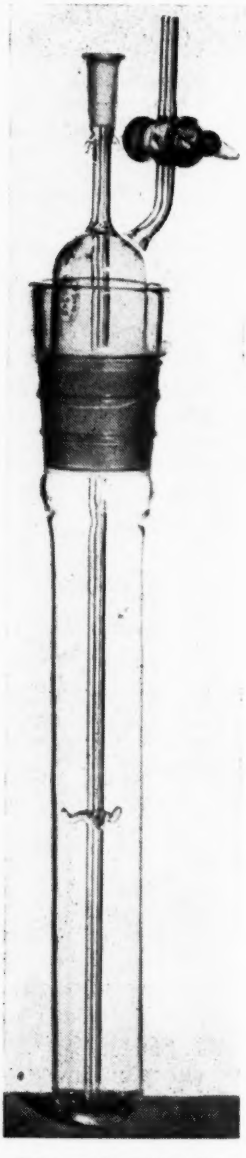

FIG. 2.—Absorption Tube

effect on the rate of absorption. After appropriate time intervals, the pressure is adjusted to 760 mm. by setting the leveling bulb at the proper differential before the next set of readings is taken.

All volume changes are calculated to a reference temperature of 25° C, and are reported as cc. of oxygen absorbed per gram of GR-S in the sample. For this purpose the observed volume of oxygen in each buret as measured at water jacket temperature is corrected to 25° C. The rest of the system remains at constant volume and temperature except for the upper portion of the absorption tubes and the capillary connecting tubes, which are exposed to the temperature of the room. Small variations due to such factors are adjusted by the use of control tubes. Any change in the corrected volumes of the control tubes can then be applied directly to the corrected volumes of each sample tube, and the difference between the resulting volume for two successive readings represents the volume absorbed.

All samples are run in duplicate tubes and the results averaged. With the apparatus described, three different samples can be studied simultaneously with the remaining two units reserved for controls. With this procedure, satisfactory reproducibility is obtained (Figure 3). These data represent

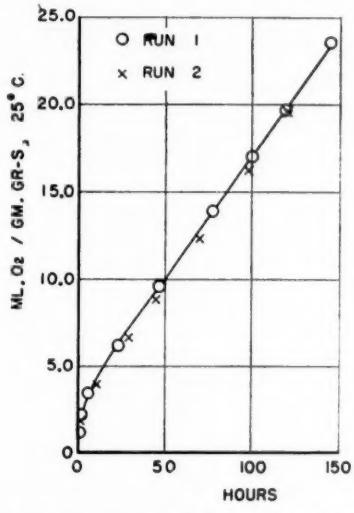

FIG. 3.—Reproducibility of Measurements (100° C, 760 Mm., Cured 50 Minutes at 298° F).

two completely separate runs, not only with respect to the oxygen absorption measurements but also separate compounding and vulcanization.

The tread type stock used had the following composition (in parts by weight):

GR-S	100.0	Zinc oxide	5.0
Bardol	5.0	Santocure	1.2
Fat acid	1.5	Sulfur	2.0
Channel black	50.0		

All samples were vulcanized 50 minutes at 298° F unless otherwise designated.

EFFECT ON PHYSICAL PROPERTIES

If oxygen absorption data are to be interpreted in terms of aging resistance, it is first necessary to correlate changes in physical properties with oxygen absorption. For this purpose rectangular specimens, 1 × 4 × (approximately) 0.026 inch were aged in the absorption apparatus at 100° C in oxygen at 760

mm. pressure. Samples (in triplicate) were removed after 1, 2, 4, and 8 days, and tensile strips were cut from each for testing. Figure 4 is a plot of tensile strength, stress at 200 and 300 per cent elongation, and ultimate elongation as a function of the amount of oxygen absorbed. The general shape of the curves is similar to that usually obtained by plotting changes in physical properties against time of aging. After the initial rapid change, the properties vary proportionally with the amount of oxygen absorbed. The plot ends at a value corresponding to an absorption of approximately 3.7 per cent oxygen by weight, based on the weight of GR-S in the sample.

The initial rapid change in both the stress at a given elongation and ultimate elongation seem to indicate either that a small amount of oxygen in the

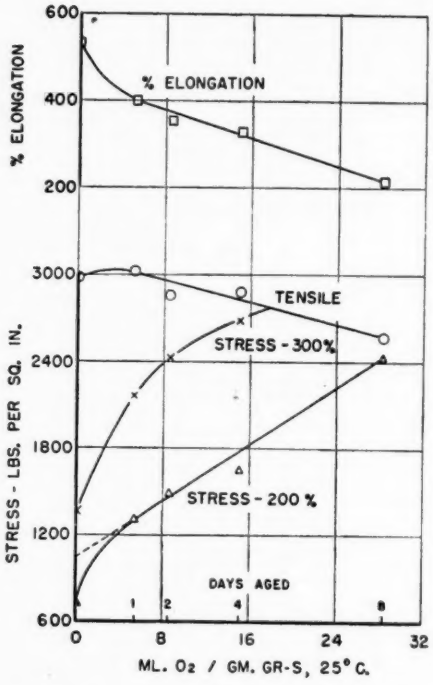

FIG. 4.—Effect of Oxygen Absorption on Physical Properties (100° C, 760 Mm.).

early stages results in structural changes which greatly affect the properties or that factors other than oxygen are also involved.

The authors showed previously[3] that approximately 45 per cent of the increase in stress at 200 per cent elongation obtained by aging 2 days in an air oven at 100° C can definitely be attributed to the action of oxygen, since only 55 per cent of the observed change in air took place in a nitrogen atmosphere. If we assume that the modulus increases regularly from the beginning with the amount of oxygen absorbed, then that portion of the observed increase which is due to other factors is represented by the intercept of the extrapolated linear portion of the curve in Figure 4. On this basis, roughly 60 per cent of the observed increase in the 200 per cent modulus after 2 days may be regarded as due to oxygen. Considering the change from air to oxygen and the experi-

mental variation in tensile, stress, and elongation measurements, this value is not inconsistent with the previously published work.

It seems probable, therefore, that the degradation of physical properties actually resulting from oxidation is at least roughly proportional to the amount of oxygen absorbed by the vulcanizate. During the first few days of aging, however, other changes (such as aftervulcanization) also occur and, thus produce a greater total change in both modulus and ultimate elongation, and a smaller change in tensile strength than would otherwise be obtained.

The close correlation between oxygen absorption data and aging data based on changes in physical properties makes possible the use of oxygen absorption as a measure of the relative aging properties of various stocks.

EFFECT OF SURFACE AREA

The rate of oxygen absorption at constant temperature and pressure could be limited by either of two factors: the rate of reaction of oxygen with the vulcanizate or the rate of diffusion of oxygen into the sample. If diffusion is a factor, the rate of oxygen absorption should increase, as the area-to-weight ratio of the sample is increased, until a point is reached where the diffusion of oxygen into the sample is rapid enough to maintain the chemical reaction at its maximum rate. Since each of these factors would be influenced differently by temperature, the effect of varying surface area for a given sample weight was

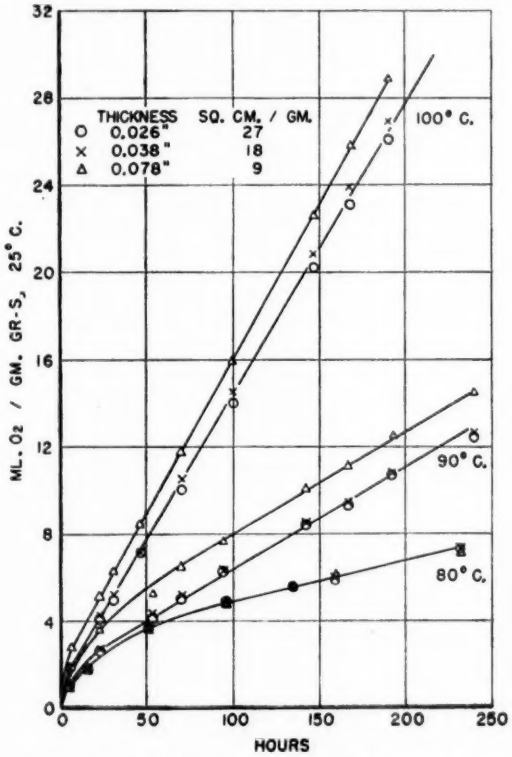

FIG. 5.—Effect of Surface Area on Oxygen Absorption at 80°, 90°, and 100° C (760 Mm., Cured 50 Minutes at 298° F).

investigated at 80°, 90°, 100°, 110°, and 120° C. In each instance samples were cut from vulcanized sheets of three different thicknesses averaging 0.078, 0.039, and 0.026 inch, respectively. The range of surface areas thus obtained was approximately 9, 18, and 27 sq. cm. per gram, respectively, so that the thin samples had three times as much surface for a given sample weight as those cut from ordinary tensile sheets.

The absorption data are plotted in Figure 5 for studies at 80°, 90°, and 100° C. All the curves show the same general type of absorption—initial rapid rise followed by a slower linear rate. At 80° the data for all three sample thicknesses follow the same curve. At 90° and 100° C the samples with lower

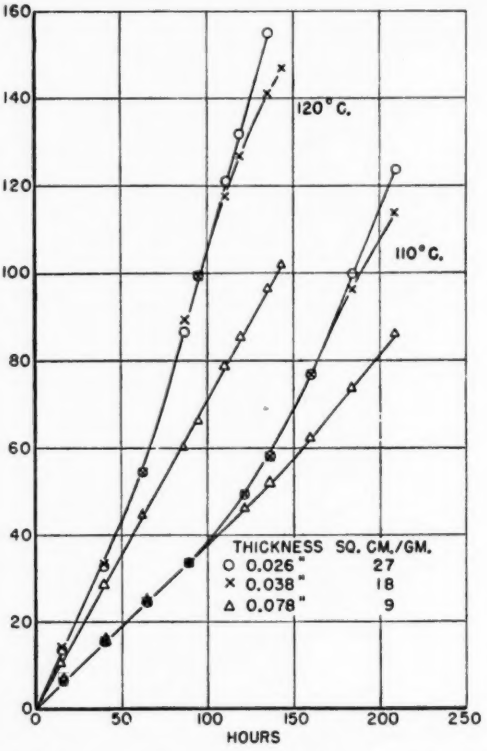

FIG. 6.—Effect of Surface Area on Oxygen Absorption at 110° and 120° C (760 Mm., Cured 50 Minutes at 298° F).

ratio of surface area to weight absorbed more oxygen during the initial stage than either of those with greater surface areas. After the first few hours, however, all samples absorbed oxygen at the same linear rate at a given temperature. Subsequent work has shown that diffusion does limit the rate of absorption during the initial rapid rise at both 90° and 100° and, consequently, the samples of greater surface area had absorbed more oxygen before the initial reading was taken. In these early studies the system was allowed to stand for about an hour to attain temperature equilibrium before the first reading was taken. In subsequent work the initial reading has been recorded immediately, and any error due to lack of temperature equilibrium is corrected by the corre-

spondingly small changes observed with the control tubes. For example, the data for the 100° C curve in Figure 8 was obtained in this manner using thin samples, and the observed absorption corresponded to the curve for the thick samples in Figure 5. It is clear that, over the range of sample thicknesses studied, diffusion is not an important factor at or below 100° C.

The absorption curves obtained at 110° and 120° C (Figure 6) appear at first glance to be somewhat different in type from those described above. These differences are discussed later under the effect of temperature.

Diffusion appears to limit the absorption rate of the thicker samples during the later stage of oxidation. There is little difference, however, between the medium and the thin samples up to an absorption of about 100 cc. per gram of GR-S. To avoid limitation of oxygen absorption by rate of diffusion, it is therefore necessary to employ thin samples (less than 0.040 inch) for studies at temperatures above 100° C, but at or below this temperature samples cut from tensile sheets of standard thickness may be used as a matter of convenience.

EFFECT OF CURE

It is well known that the initial state of cure has a pronounced effect on aging as measured by changes in physical properties. Since it has also been shown[3] that oxygen plays a major part in aging, it seemed desirable to determine the effect of cure on the rate of oxygen absorption.

The samples for this study were cut from tensile sheets of standard thickness, vulcanized for 20, 40, and 80 minutes at 298° F. The physical properties of these vulcanizates showed that 20 minutes gave an undercure, while 80 minutes produced an overcure. Figure 7 gives the oxygen absorption data obtained at 100° C.

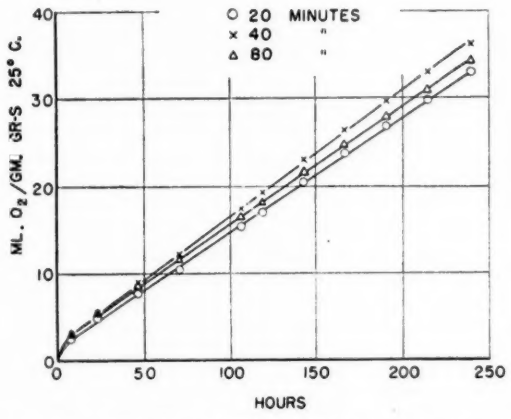

FIG. 7.—Effect of Cure on Absorption at 100° C and 760 Mm. (Platen Temperature, 298° F).

The effect of cure was unexpectedly small when compared to the marked effect observed by Kohman[5] with natural rubber, in which case the rate of oxygen absorption increased with time of cure. With GR-S, on the other hand, the effect is not only small, but the overcure absorbed oxygen at a slightly lower rate than the 40-minute cure. This is in line with the greater resistance of GR-S overcures to oven aging as observed by Harrison and Cole[6]. It is of

interest to note (as further evidence that the unusual order shown in Figure 7 is nevertheless real) that the curve obtained for a 50-minute cure of comparable surface area (Figure 5) lies between the curves for the 40- and 80-minute cures when plotted on the same graph.

Since time of cure produces so little effect on the rate of oxygen absorption, this apparatus and technique may well prove to be superior to the more conventional methods for evaluating antioxidants and the effect of various other compounding ingredients upon aging. Such studies usually involve the measurement of changes in physical properties, and the effect of variations in compounding on cure frequently obscures the effect on aging resistance. If oxygen absorption methods were used, however, such difficulties would be avoided, since cure has so little effect on rate of oxygen absorption by GR-S.

EFFECT OF TEMPERATURE

The effect of temperature on the rate of oxygen absorption by GR-S is demonstrated in Figure 8. The curves were plotted from the data obtained

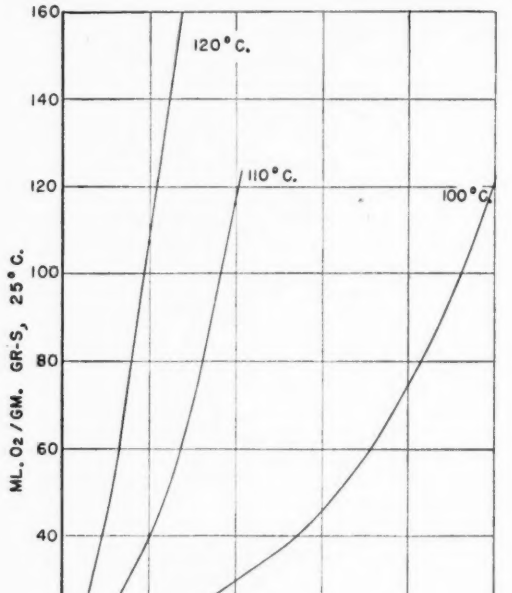

FIG. 8.—Oxygen Absorption at Various Temperatures (760 Mm., Cured 50 Minutes at 298° F).

with the thin samples, so diffusion is not a factor in this case. The curve for 100° C is typical of a vulcanized GR-S tread stock, since it includes all the special features of the curves obtained at both lower and higher temperatures. This curve indicates that three distinct stages are involved: an initial rapid

rise, a slower constant rate period, and a final upswing which approaches a a linear rate of greater magnitude.

The initial rapid rise observed at 80°, 90°, and 100° C is not detectable at the two higher temperatures, but apart from this initial rise all the curves show a linear absorption rate up to the point at which the upswing occurs. This upswing in the curves for 100°, 110°, and 120° C occurred after each had absorbed approximately 40 cc. of oxygen per gram, or roughly 5 per cent by weight, based on the weight of polymer in the compounded stock. The absorption at 80° and 90° C would, in all probability, show a similar upswing if the measurements were continued for a sufficient time. The fact that the break occurs after a constant amount of oxygen has been absorbed is consistent with either the building up of a sufficient concentration of peroxides to start an autocatalytic reaction or with the depletion of the antioxidant at that point.

The general form of these curves is similar to that observed by Kohman[5] with natural rubber except that his curves do not show an initial rapid rise, and the linear rate is much more rapid than with GR-S. Kohman's experiments were carried to a more advanced stage of oxidation, in which the rate decreased as the oxidizable rubber concentration diminished. A similar behavior could probably be demonstrated with GR-S by continuing the measurements for a longer period. A suggestion of such a decrease in rate was, in fact, indicated by the last point (not shown) in the case of the 120° C curve of Figure 8. However, the material was so hard and brittle that it was completely worthless at the termination of the runs reported here, and it was therefore decided to confine the present study to the earlier stages of oxidation.

The difference between the oxidative behavior of GR-S and natural rubber is marked; however, the authors have come to the conclusion that the difference is primarily a matter of degree and relative rates rather than a fundamental difference in the nature of the reactions involved. Reactions resulting in chain scission (as shown by tensile breakdown) and in hardening (as shown by increased modulus) occur in both cases; but the former predominates in natural rubber, while the latter predominates in GR-S, and the overall rate of oxidation of natural rubber is much the faster.

THEORETICAL CONSIDERATIONS

The preceding section showed that there are three distinct stages in the oxygen absorption curve for a typical GR-S tread stock. The physical properties of the stock are degraded, as oxidation proceeds, to such an extent as to be of little practical value even before the final upswing is reached. For this reason the following discussion is limited to the first two stages. It should be pointed out, however, that the third stage is apparently an autocatalytic reaction similar to that observed with natural rubber.

The rapid absorption observed in the initial stage could be caused by either chemical reaction or physical absorption resulting from increased solubility of oxygen in GR-S when the sample is transferred from air to an oxygen atmosphere. To test the latter theory, samples were placed in oxygen under a gauge pressure of 300 pounds per square inch and left overnight at room temperature. The samples were thus supersaturated with oxygen when removed from the bomb and placed in the absorber at 100° C. If physical absorption were the true explanation, no initial rapid rise would be expected under these conditions, but rather a lower initial rate followed by the constant rate characteristic of the second phase of the reaction. Figure 9 shows the actual behavior observed

for these samples as compared with control samples handled in the usual fashion. After the first hour, during which the excess oxygen escaped, the curves are almost identical in form.

The initial rapid absorption of oxygen must, therefore, represent a chemical reaction. Since this initial rate soon levels off as it approaches the slower constant-rate reaction, it would appear that the particular reaction responsible for the initial rapid absorption is completed within the first few hours at 100° or days at 80° C.

For the purpose of developing a theoretical equation for the absorption of oxygen by GR-S, we shall assume the existence of a limited number of particularly reactive centers which are attacked rapidly by oxygen and thus are responsible for the initial rapid absorption. Such active centers might result from certain special structural relations between double bonds and phenyl groups due to: (1) the uneven distribution of styrene units, (2) the polymerization of butadiene in the 1,2- as well as the 1,4-position, and (3) the probable existence of both *cis* and *trans* isomers (3). Whatever their nature, however,

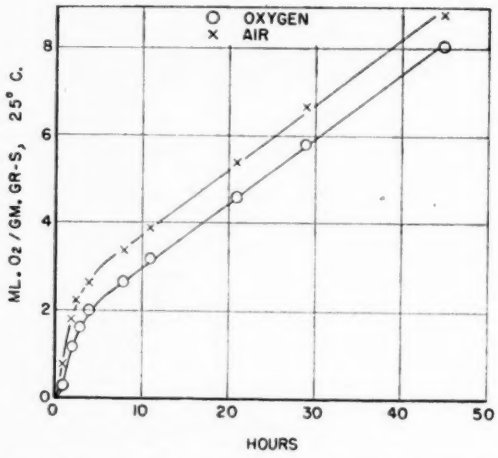

FIG. 9.—Effect of Previous Saturation on Oxygen Absorption (100° C, 760 Mm., Cured 50 Minutes at 298° F).

once these especially reactive centers have been oxidized, the absorption rate becomes linear as oxidation about the normally situated double bonds proceeds at a steady rate.

The above theory is only one possible explanation of the presence of "active" as well as normally reactive centers in the vulcanizate. Other plausible mechanisms include the activation of certain preferentially absorbed groupings on the surface of the carbon black, the presence of sulfur in certain readily oxidizable forms, and the combination of oxygen with the antioxidant. The following theoretical analysis is based only on the existence of both particularly active and normally reactive centers, and is valid regardless of the reason for the greater than normal reactivity.

If the normal constant-rate reaction proceeds from the start, then the total volume of oxygen absorbed at any time, t, is the sum of that required for reaction with the normal and the active structures. In Figure 10 the extrapolation

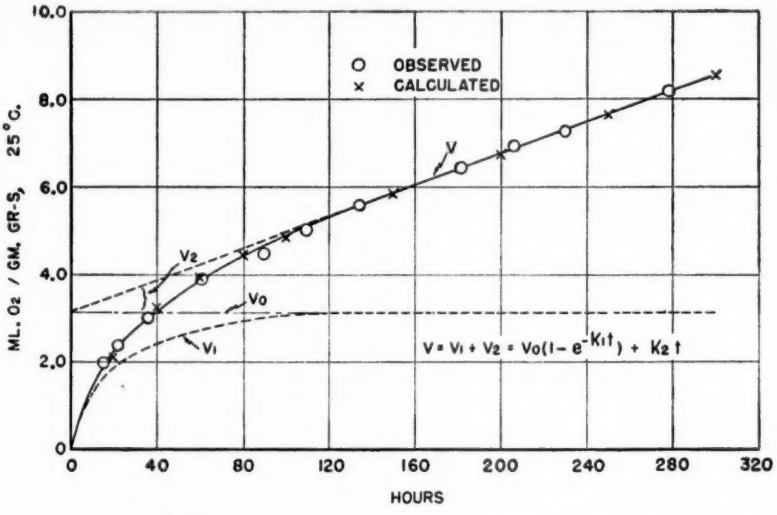

FIG. 10.—Analysis of Oxygen Absorption Curve (80° C, 760 Mm., Cured 50 Minutes at 298° F).

of the straight-line portion of the curve to zero time, therefore, gives the volume of oxygen required to react completely with all active centers. If we assume:

V = volume of O_2 (25° C and 760 mm.) absorbed at time, t
V_1 = volume of O_2 absorbed by reaction with active centers
V_2 = volume of O_2 absorbed by reaction with normal structures
V_o = total volume of O_2 required to react completely with all active centers
then $V = V_1 + V_2$
$V_o - V_1$ = effective concentration of active groups remaining at any time, t

$$dV_1/dt = K_1(V_o - V_1) \tag{1}$$

$$dV_2/dt = K_2 \tag{2}$$

where K_1 and K_2 are the rate constants for the active and normal reactions, respectively. By integration we obtain:

$$V_1 = V_o\,(1 - e^{-K_1 t}) \tag{3}$$

$$V_2 = K_2 t \tag{4}$$

$$V = V_o\,(1 - e^{-K_1 t}) + K_2 t \tag{5}$$

To test the validity of Equation 5, the constants were evaluated from the experimental data and the calculated absorption was compared with that observed at 80° C in Figure 10. On this plot the actual experimental absorption curve is drawn as a solid line, the experimental points are circled, and the extrapolated portion of the straight line (the slope of which is K_2) is shown as a dashed line whose intercept gives the value of V_o. The curve for V_1 was determined graphically by subtracting V_2 from V (where V_2 is the difference between the extrapolated portion of V and V_o). This curve approaches V_o as a

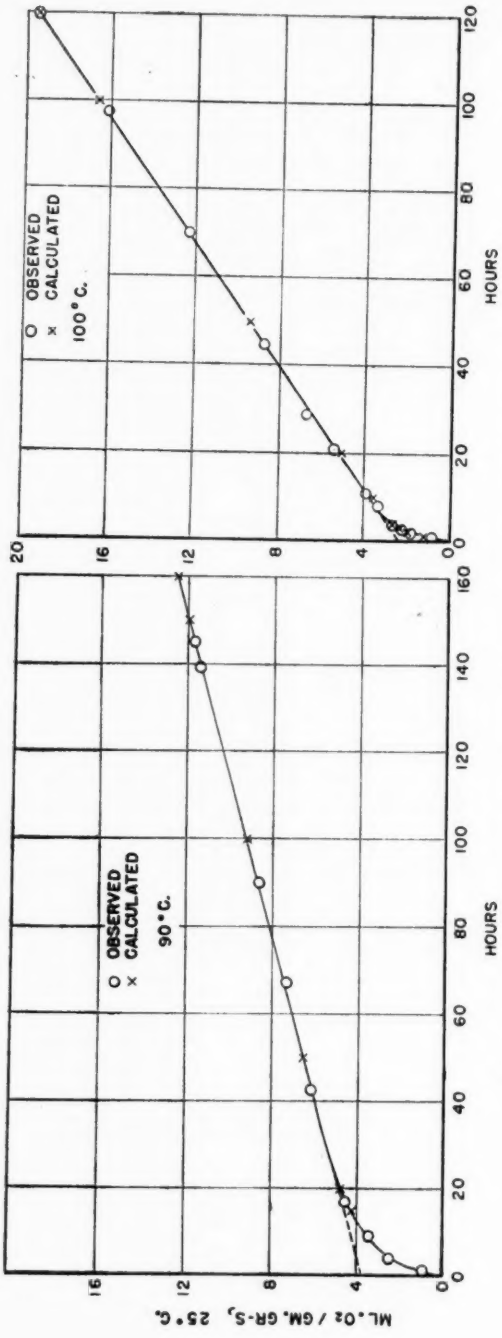

FIG. 11.—Correlation of Observed and Calculated Absorption (760 Mm., Cured 50 Minutes at 298° F).

limit. At various values of t, corresponding values of V, V_1, and V_2 were determined from the curve and K_1 was calculated according to Equation 3. The average of these values was employed to calculate the points plotted as crosses. Similar comparisons of observed and calculated oxygen absorption are shown in Figure 11 for absorption at 90° and 100° C.

The close agreement between the calculated values and the experimental data clearly justifies the theoretical assumptions on which the derivation was based and establishes the apparent order of the reactions involved in the first two stages. Under the conditions of the test (constant oxygen pressure) the initial reaction with the active centers behaves as a first-order reaction. The observed linear rate for the second stage justifies the assumption that the change in concentration of the remaining oxidizable groups is too small to affect the rate over the range involved. Thus, at constant oxygen concentration it takes the form of a zero-order reaction.

The following tabulation summarizes the constants evaluated from the data obtained at the five temperatures:

Temp. (° C)	V_0	K_1	K_2
80	3.13	0.040	0.018
90	3.72	0.157	0.055
100	2.20	0.613	0.144
110	..	..	0.382
120	..	..	0.817

Theoretically V_0 is a constant for a given stock; however, the experimental value may vary somewhat, depending on the amount of oxidation which the active centers have undergone at the time of the initial reading. It should be independent of temperature except as the increased rate of reaction at the higher temperatures makes it increasingly difficult to obtain an initial reading at the true zero of time, and the increased rate of the second stage (Figure 8) causes it to merge with the first. At temperatures above 100° C, V_2 becomes so much greater than V_1 that the first term of Equation 5 may be neglected.

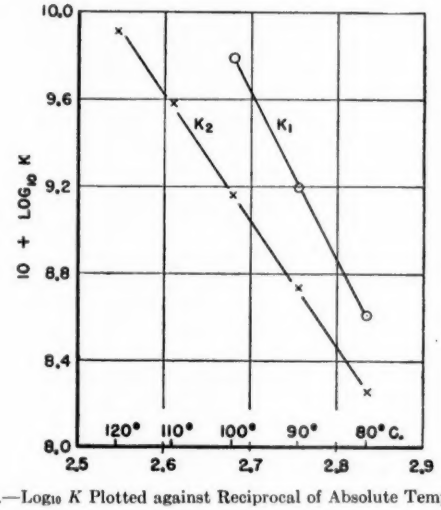

FIG. 12.—Log$_{10}$ K Plotted against Reciprocal of Absolute Temperature

The plot of log K against the reciprocal of absolute temperature in Figure 12 is a straight line for both K_1 and K_2, indicating that single reactions are rate controlling in both cases. The temperature coefficients are 3.9 and 2.6, respectively, for a 10° C change in temperature over the range 80° for K_1, and 80° to 120° for K_2. The figure 2.6 is in good agreement with values previously reported for the deterioration of physical properties for both natural and synthetic rubber during aging, which range from approximately 2.0 to 2.6[6]. The much higher value of the temperature coefficient for K_1 indicates a higher energy of activation for the initial reaction.

The energy of activation, E, may be calculated by the integrated form of the Arrhenius equation:

$$\ln \frac{K'}{K} = \frac{E}{R}\left(\frac{T' - T}{T'T}\right)$$

For the first reaction—that is, the initial rapid rise—the energy of activation is 36,000 calories; for the second or linear reaction, it is 26,000 calories. These values are too large for a physical process and clearly represent a chemical reaction of oxygen with the GR-S vulcanizate.

It should be recognized that the absorption rates reported in this paper apply only to the particular stock employed. However, the effect of the variables studies should be similar for any GR-S vulcanizate.

SUMMARY AND CONCLUSIONS

Oxygen absorption studies on a tread type GR-S vulcanizate show:

1. There are three stages involved in the oxidation: (1) an initial rapid absorption, of apparent first order at constant pressure, which is of short duration and appears to involve a limited number of especially reactive centers in the vulcanizate; (2) a constant-rate reaction, of apparent zero order at constant oxygen pressure, which would extend over most of the useful life of the vulcanizate in service; (3) an autocatalytic reaction, beginning after a given stock has absorbed a definite amount of oxygen that is independent of the temperature at which the absorption takes place.

2. The rate of oxygen absorption increases with temperature. The temperature coefficient for the constant rate reaction is 2.6 for a 10° C change in temperature over the range 80° to 120° C.

3. Diffusion is not rate controlling, provided the specimen thickness does not exceed 0.080 inch at 100° C or 0.040 inch at 120° C.

4. The effect of cure on the rate of oxygen absorption by GR-S vulcanizates is slight, and consequently, the technique is particularly useful for studying the effect of changes in compounding upon aging resistance.

5. Oxygen absorption data can be satisfactorily correlated with changes in physical properties during aging.

While the fundamental nature of the mechanism of the oxidation of GR-S is still unknown, considerable information has been obtained with respect to some of the factors involved, and the general nature of the reaction has been established. This information, together with the work still in progress, should be of value in pointing the way toward possible methods of improving the resistance of GR-S to aging.

ACKNOWLEDGMENT

The authors desire to express their thanks to The Firestone Tire & Rubber Company for sponsoring this work and for permission to publish this portion of the data; Hugh Winn is Firestone Fellow at Case School of Applied Science. The authors are particularly grateful to O. D. Cole of Firestone and to C. F. Prutton and David Turnbull of Case School of Applied Science for helpful suggestions and cooperation.

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WEATHERING OF SOFT VULCANIZED RUBBER *

JAMES CRABTREE AND A. R. KEMP

BELL TELEPHONE LABORATORIES, INC., MURRAY HILL, N. J.

When rubber goods are exposed to the agencies which constitute "weather", they undergo profound changes. The rubber may lose elasticity, it may split or crack, or the surface may take on a crinkled appearance in a wide variety of designs. Figure 1 shows a small selection of such weathered rubbers. The course of deterioration, or the ultimate condition of any particular rubber specimen, moreover, is not always the same, but depends to a considerable extent on the kind of weather encountered which, in turn, depends on geography, topography, and season. The components of weather are air, heat, water, and sunlight, each varying in quantity and quality so that infinite combinations are possible.

Among the major (nitrogen and oxygen), minor (carbon dioxide, argon, helium, neon, krypton, xenon), and trace (ozone, nitrogen oxides, ammonia, sulfur dioxide, sulfuric acid, hydrogen sulfide, carbon monoxide, hydrocarbons, hydrogen, mineral salts, hydrogen peroxide, organic peroxides) components of the atmosphere, only oxygen, ozone, and nitrogen oxides are capable of reacting with rubber. Trial shows steadily that, of these, only oxygen and ozone produce any perceptible effect at the concentrations in which they are present.

Heat alone, within the limits experienced in ordinary weathering, occasions no permanent changes, nor does water alone, in either the vapor or liquid phases, play any outstanding role. They are to be considered, therefore, only in conjunction with other forces.

Sunlight is the most obvious component of weather. Perhaps this is one reason why artificial weathering devices are almost always mechanical systems built around a source of light whose intensity is periodically raised to increasing levels by the zealous designer. This paper will show that, of the weathering agencies, the only ones of major importance are light, oxygen, and ozone. Their resultant effects depend on the nature of the rubber compound, the relative preponderance of these factors, and the temperature at which they operate.

Since sunlight not only promotes the oxidation of rubber but is also responsible for the presence of ozone, it is desirable to review the following facts. The spectrum of sunlight outside the earth's atmosphere is radically different from that at the surface of the earth—a result of preferential scattering by the molecules of gas comprising the atmosphere and by dust, and of absorption by atmospheric gases and vapors, notably water, ozone, oxygen, and carbon dioxide. The thicker the layer of atmosphere penetrated, the greater is the difference (Figure 2). The chief concern here is the progressive removal of the ultraviolet component (below 4000 Å.). Scattering by dust and absorption by water and ozone vary widely from hour to hour, day to day, month to month, and place to place. Figure 3 gives an idea of the hourly and seasonal changes in the ultraviolet fraction of solar energy at the earth's surface. Obviously sunlight is variable both in quantity and quality.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 38, No. 3, pages 278-296, March 1946.

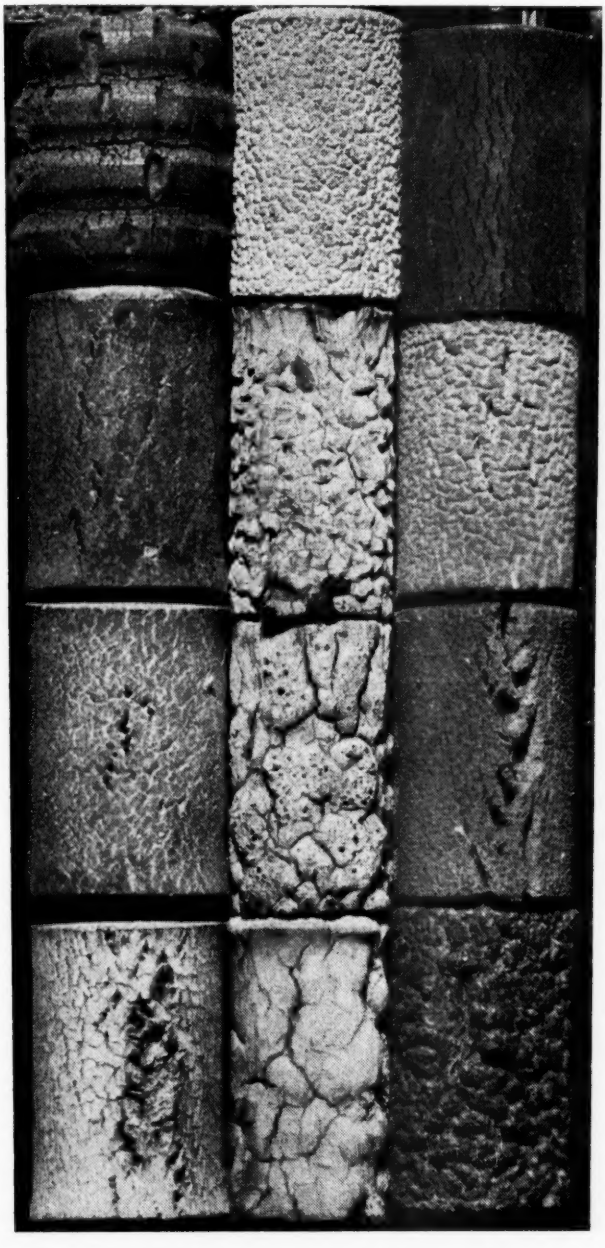


FIG. 1.—Types of Physical Change Resulting from Exposure to Weather of Soft Vulcanized Natural Rubber Compounds

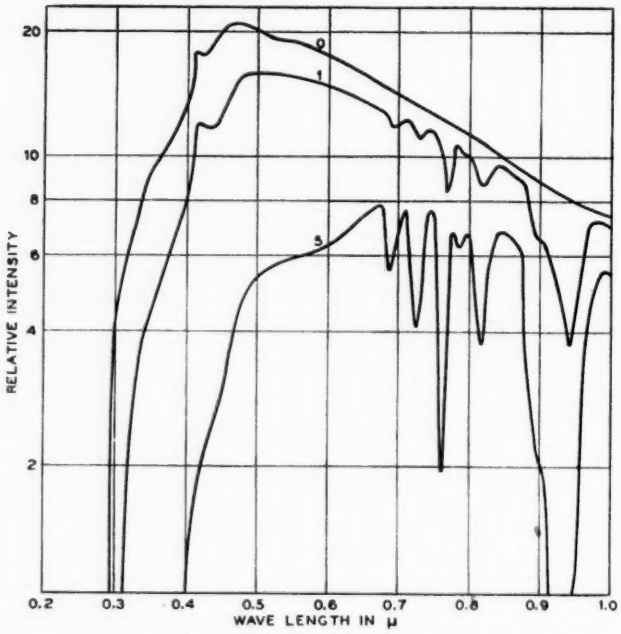


FIG. 2.—Spectral Distribution of Color Radiation[1]

0. Outside the atmosphere
1. Air-mass 1 (sun at zenith)
5. Air-mass 5 (sun near horizon)

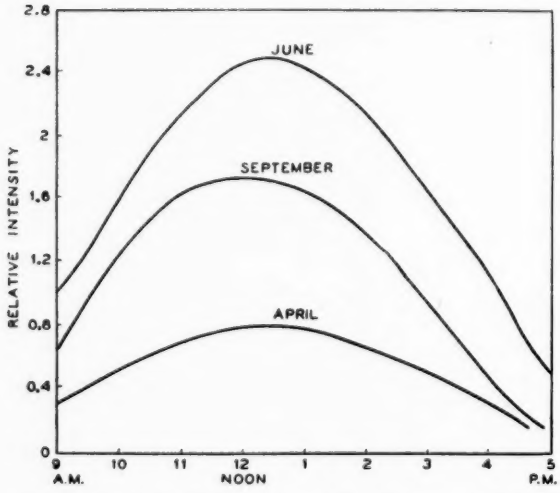


FIG. 3.—Changes in Ultraviolet Component of Sunlight with Season and Hour of Day[17].

EFFECT OF LIGHT

When light falls on an object, it is either transmitted, reflected, or absorbed. When absorbed its energy may be transformed in various ways. It may be re-emitted as fluorescence; or the molecules which have absorbed the light, having attained a higher energy or "excited" state, may enter into chemical reaction or may dissociate; or the absorbed energy may be degraded by various processes into heat energy.

When radiation is absorbed by an organic material, certain wave lengths may be absorbed preferentially, depending on the structure of the molecule; the plot of such absorption against wave length is characteristic of the material.

All light is not equally effective, since the energy in a quantum of radiation varies inversely as the wave length; that is, the shorter the wave length, the greater the energy. For this reason ultraviolet radiation is more effective in promoting chemical change than is visible light, and infrared radiation is incapable of initiating such change. Moreover, since a definite amount of energy is required to raise a given molecule to a reactive state, there is a certain wave length above which light is not able to promote chemical change in that molecule, no matter how much of such light be used and whether it be absorbed or not.

Published data on the absorption of light by vulcanized rubber are meager. Scheibe and Pummerer[2] and others[3] report a strong absorption band in purified rubber hydrocarbon around 2000 Å. (which region is absent from sunlight) and continuous absorption at longer wave lengths. Wood[4] gives curves of absorption in the visible range, showing continuous absorption which gradually increases with decrease of wave length. Figure 4 gives curves of absorption

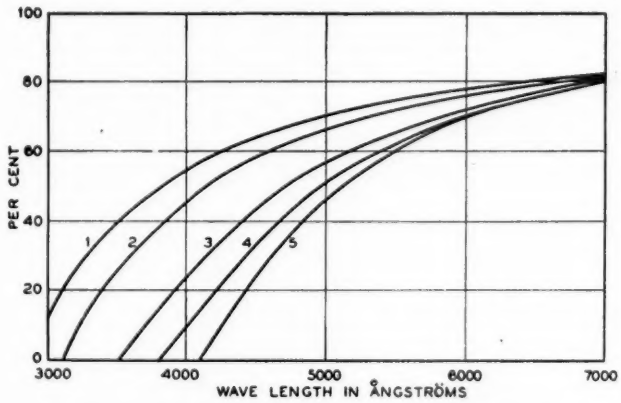


FIG. 4.—Spectral Transmission of Natural Rubber (0.1 Mm. Thick)

1. Smoked sheets
2. Base compound unvulcanized
3. Vulcanized 5 minutes at 60 lb./sq. in.
4. 15 minutes
5. 60 minutes

from measurements by the authors, for crude rubber (smoked sheet) used in the experiments to be described here, through the visible and ultraviolet range of sunlight. These, together with the published data referred to, show that pure rubber hydrocarbon exhibits only a moderate increase of absorption of sunlight's ultraviolet compared with the visible, that this is increased by the im-

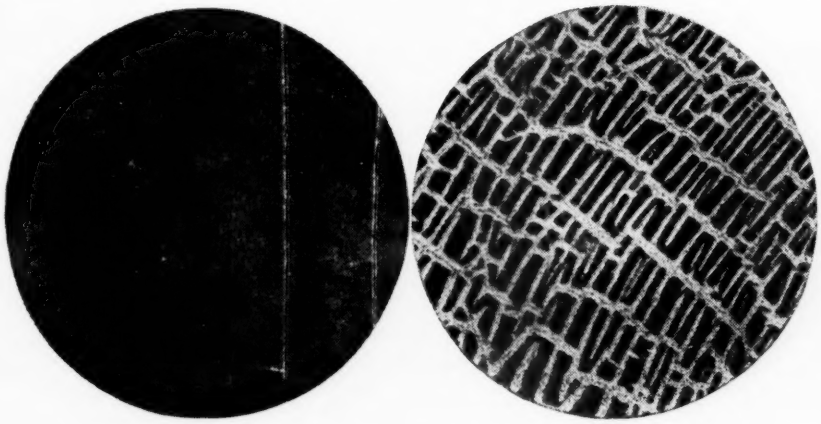
purities of raw rubber, that further increase results from the antioxidants and accelerators in compounding, and that vulcanization augments it still further, until at optimum cure practically all the ultraviolet and much of the violet and blue are totally absorbed by a very thin film. Further vulcanization results in the absorption of progressively longer wave lengths, as shown by the deepening in color from yellow to brown to almost black in the case of ebonite. It does not necessarily follow, however, that any chemical action resulting from light absorption follows the same curve. The wave length at which this begins is still not certain. Asano[5] states that raw rubber oxidizes in air under the influence of light below 5000 Å.; in the case of the light-energized oxidation of fats and oils which is closely analogous to that of rubber, Greenbank and Holm[6] found little effect at wave lengths greater than 5000 Å. and progressive increase at shorter wave lengths.

Many workers have inquired into the changes resulting when rubber (mostly unvulcanized) is exposed to radiation, visible and ultraviolet. Ellis, Wells and Boehmer[7] give a useful review. Most of this work is, however, of little help to the technologist in reaching an appraisal of the gross result of exposure to weather. Some of the observations to be described were made by previous observers, but they have been repeated or extended for confirmation and to fill out the picture. In these studies only those frequencies of radiation present in sunlight have been employed. Although light absorption by rubber is more pronounced in the ultraviolet, the total energy in this component of sunlight amounts to less than 10 per cent of that of the visible component. The sources of light used were General Electric S_1 and S_4 sun lamps, Eveready arc with Sunshine carbons filtered through Corex D, Pyrex, or window glass, and sunlight itself.

Since smoked sheet is the most commonly used form of raw rubber, it was studied in practically all the compounds reported here. The base compound was: smoked sheet 100, sulfur 3, zinc oxide 2, Neozone A 1, and di-*o*-tolylguanidine 1. When such a compound (or variants incorporating the usual run of fillers, softeners, etc.) is exposed to sunlight in an atmosphere of oxygen-free nitrogen for long periods, the irradiated surface darkens somewhat and acquires a thin inelastic coat. The darkening is due, not to the rubber hydrocarbon, but to changes in the nonrubber components (impurities and antioxidants). Infrared absorption measurements by the authors suggest that this kind forms as a result of polymerization. The change is slight, however, and negligible compared to the changes which occur when oxygen is present. The change in weight is nil, and there is little loss of tensile strength. The presence of moisture does not affect the picture.

In the presence of air or oxygen, darkening is increased, and a hard, shiny inelastic skin formed rapidly at the illuminated surface, accompanied by a progressive absorption of oxygen, increase in weight, and loss of tensile strength. A thin sheet thus exposed for long periods in a relaxed condition finally assumes a saucerlike shape with the concavity of the exposed side, an indication of diminution in volume of the surface layer. Ultimately, long fine cracks may appear, but usually the familiar checking or cracking of weathered rubber is not seen. If the sheet is thin enough and transparent so that light may permeate the mass, the whole sheet becomes hard and brittle. Exposed in a stretched condition, the result is the same except that, when degradation is far advanced, the strip may break into two pieces under the slight remaining strain. The total length of the hardened strip is, however, practically the same as its initial stretched dimension. The break appears the sooner, the lower the rub-

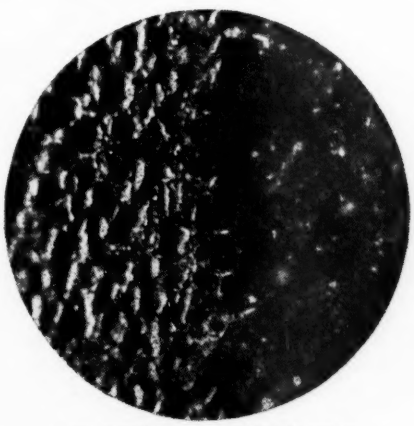
ber content of the compound. At no time, however, do multiple cracks of the type usually referred to as light cracking appear. On leaching in water, brown soluble components are lost to the extent of approximately 15 per cent of the gain in weight resulting from exposure. In undercured specimens this loss is greater. If leaching is done at intervals during the exposure, the texture of the surface undergoes a gradual change, and a criss-cross pattern of shallow fissures gradually takes shape, and culminates in the familiar checked or crazed appearance (Figure 5). The kind of pattern produced, however, is not always



No water Water

FIG. 5.—Effect of Periodical Leaching with Water of Vulcanized Soft Rubber Exposed to Light and Air (×7)

typical of the compound, but may be altered by changing the conditions. If the light is intense and the rubber partially transparent, the outer skin is rapidly formed, and assumes sufficient rigidity to retain its shape in spite of subsequent leaching or changes in temperature, as shown in Figure 6. The



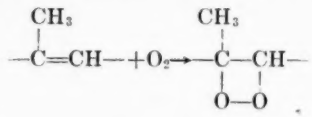
Low intensity High intensity

FIG. 6.—Effect of Intensity of Light Exposure on Surface Checking (×7)

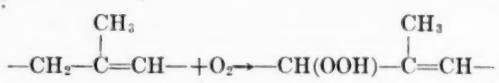
latter is a photograph of a compound of high rubber content exposed to the light from a carbon arc and sprayed with water every 2 hours. The smooth portion received the full intensity, but the checked portion was screened behind a piece of ground glass. In outdoor weathering the kind of filler is the major factor which determines the resulting pattern, since the filler affects the physical properties of the compound and also the rate of oxidation. Checking, then, is due to oxidation of the surface, accompanied by a change in volume and a gradual "forming" of this surface by leaching, erosion, and "working" by dimensional changes of the underlying rubber mass.

THEORY OF UNVULCANIZED RUBBER

This paper is not concerned with the difficult and involved mechanism of the reaction between rubber and oxygen, but only with the resulting gross observable changes. Nevertheless, brief reference will be made to recent theory as far as unvulcanized rubber is concerned. Rubber, in common with other olefins, absorbs molecular oxygen, and there is little doubt that the first stage of this autoöxidation is the formation of peroxide groups. It has usually been assumed that the oxygen adds at the double bonds in a simple additive reaction:



with the resulting loss of unsaturation commensurate with the degree of oxygen intake. Farmer and his collaborators[8], however, find no loss of unsaturation in the alpha position to the double bonds and there forms unstable hydroperoxide groups:



These groups then decay, and the active oxygen thus furnished serves for attack at the unsaturated centers. The result may be chain scission at the double bonds or saturation of the double bond without its severance. If this mechanism is correct, light may function by activation of the rubber by previous dissociation of the isoprene unit at the α-methylenic carbon-hydrogen bond.

In the case of unvulcanized rubber, decrease in molecular weight with loss of viscosity and increase in tackiness follow; in vulcanized rubber the trend is to resinification, so the secondary reactions in this case obviously lead to different end products, probably by condensation.

OXIDATION RATE

The conditions which effect the rate of oxidation of rubber compounds have been studied by following the increase in weight of a sheet (0.025 inch thick) of the compound, moulded in a standard 6-inch chromium-plated mould and subjected to the conditions under study. The difference between the weight of gaseous oxygen absorbed and the increase in weight of the exposed specimen is so small compared to the total weight gained that it may be neglected for present purposes[9]. This gravimetric method simplifies the experimentation enormously. A strip of the compound, 1.5 to 4 inches wide and 6 inches long (depending on the kind of test) was conditioned in a desiccator, weighed, and

exposed, free or tacked to a blackened board, in the open or enclosed in a quartz, Vycor, or Pyrex vessel (depending on the source or circumstances) containing air or oxygen. When exposure was made to an artificial source, the specimens were mounted vertically on a rotating cylindrical framework with the source on the axis, the distance from the source being 12 to 24 inches. After exposure, samples were reconditioned in the desiccator and reweighed. The dark reaction was determined in all cases by duplicate exposure shielded from light behind a mask of thin black paper. This method leaves something to be desired since the temperature of the illuminated surface of a rubber specimen is always higher than the ambient temperature; the darker the color of the specimen, the higher is the temperature when illuminated. By these means the influence of the following factors was studied.

Humidity.—Specimens exposed in closed vessels containing oxygen over P_2O_5, $CaCl_2$, a saturated solution of $Na_2Cr_2O_7$ (50 per cent relative humidity) or water (100 per cent relative humidity) showed no differences in weight gain.

Temperature.—Differences in temperature under otherwise identical exposure conditions were secured by binding the thin samples to glass tubes through which water was circulated. The temperature of the specimens was assumed to be that of the water; this assumption is not quite correct, since the illuminated surface was undoubtedly hotter than the rear surface. However, the temperature differential is probably not far out of line. The following results are typical:

		Increase in weight (percentage)	
Cold (° C)	Hot (° C)	Hot over cold	Per 10° C
27	82	160	30
21	61	130	32

The comparatively low temperature coefficient is characteristic of light-energized reactions.

Elongation.—Specimens stretched up to 100 per cent elongation showed increases in weight proportional to the resulting increase in area in gum compounds, but somewhat less in compounds containing light colored fillers (whiting, for example). In the latter case, stretching increases the reflectance and thus reduces the light absorbed and the amount of oxidation. This degree of tension, therefore, does not influence the rate of the light reaction to any appreciable amount.

Thickness.—Light-energized oxidation of rubber proceeds more rapidly in thin specimens than in thick. Weight gain was, for example, approximately 50 per cent more rapid in 0.010-inch than in 0.100-inch sheets; this was probably due to the more ready penetration of air into the thinner sheet as a result of the greater surface area per unit of mass. This reasoning is supported by the fact that light-energized oxidation proceeds in oxygen at approximately three times the rate in air. Thus, thin rubber goods exposed to light and air deteriorate at a proportionally greater rate than thick ones.

Antioxidants.—While antioxidants differ in degree of effectiveness, most of them cause an appreciable decrease in the light reaction. For example, specimens 9 square inches in area and 0.025 inch thick were exposed for 6 days in oxygen to the S_4 sun lamp. The weight gains (in grams) with various percentages of Neozone A present follow:

	None	1%	2%	5%	10%
In light	0.102	0.030	0.023	0.018	0.008
In dark	0.005	0.004	0.004	0.003	0.001

State of Cure.—Figure 4 shows that a progressive increase of light absorption of the shorter wave lengths occurs as the state of vulcanization increases. That the rate of thermal oxidation increases with increase in time of vulcanization is well established[10]. It is not surprising, therefore, that the light reaction also increases; for example, 9 square inches of the base compound in oxygen exposed to a carbon arc for 70 hours showed the following increases in weight:

Minutes vulcanization at 60 lb. per sq. in.	5	10	15	20	40
Weight grain (gram)	0.066	0.076	0.094	0.098	0.117

The same compound, but with 10 per cent sulfur and vulcanized for 60 minutes, increased 0.308 gram in weight. The water-soluble fractions of the increases were, however, very different:

Vulcanization (min.)	5	10	15	20	40	60
Percentage water-soluble	30	20	17	16	15	14

These figures suggest a progressive change in the nature of light oxidation as vulcanization increases. This difference in response to leaching by water naturally results in a difference in behavior on outdoor exposure; checking of the surface proceeds more rapidly in the case of the more lightly cured specimens (Figure 7).

Wax.—Incorporation of wax gives some degree of protection, depending on the type of compound. This was not due to any filtering of the light, since the wax transmitted practically all ultraviolet and visible light in a film of the thickness involved. It operated perhaps by enhancing the gloss and, thus, the light reflectance. In the following examples the figures are for gains in weight due to light exposure in air compared with that of "no wax" taken as 100.

Base Compound +50 Parts by wt. of:	No wax	Heliozone 1%	Heliozone 2%	Heliozone 4%
TiO_2	100	83	73	63
Crushed quartz	100	94	86	82
Whiting	100	92	92	90
Mineral rubber	100	100	95	92

Softeners.—The role of softeners has not been studied quantitatively. However, in bent specimens of low rubber content (30 per cent) undergoing light-energized oxidation, those compounds containing softeners (such as mineral rubber, oils, waxes, etc.) will, when the elongation is 50 per cent or more and the degradation is sufficiently advanced, rupture at the point of maximum curvature; the same compounds without softener continue to harden while retaining their shape.

When specimens are exposed as loops 0.075 inch thick (A.S.T.M. method), the result depends on whether the loop is free or held around a mandrel. Since the top of the loop receives most exposure, the rubber there weakens before the sides. The side tension now forces the top of the loop into a sharper and sharper bend until the strain may become sufficient to rupture the specimen. In a comparison of compounds, this effect weights the test to the disadvantage of the poorer members. Insertion of a mandrel of the correct size maintains the curvature constant and obviates the error.

Fillers.—A number of modifications of the base compound, as well as a selection of compounds in industrial use, have been compared as to rate of oxidation under identical conditions of exposure. Figures 8 and 9 show the

FIG. 7.—Effect of State of Cure on Type of Surface Checking (×7)

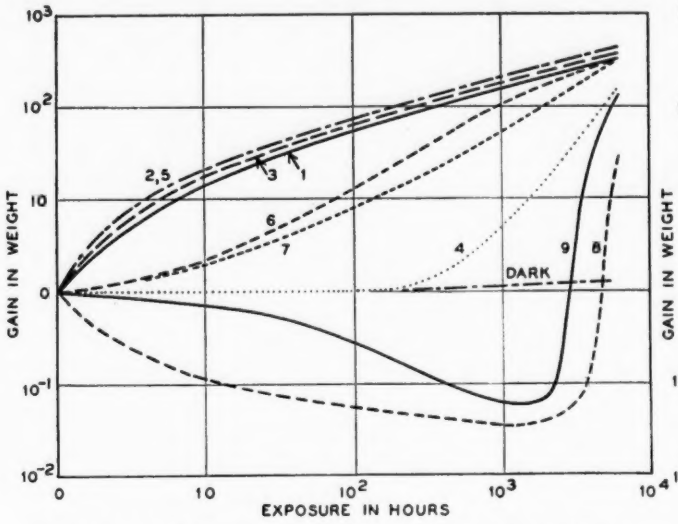


FIG. 8.—Gain in Weight (Mg. per Sq. Dm. of Surface) of 0.025-Inch Thick Sheets of Compounds Exposed in Air to a G.E.S1 Sun Lamp

1. Base compound
2. Base compound + whiting (30 parts by weight)
3. Base compound + crushed quartz (30 parts by weight)
4. Base compound + carbon black (10 parts by weight)
5. Base compound + mineral rubber (10 parts by weight)

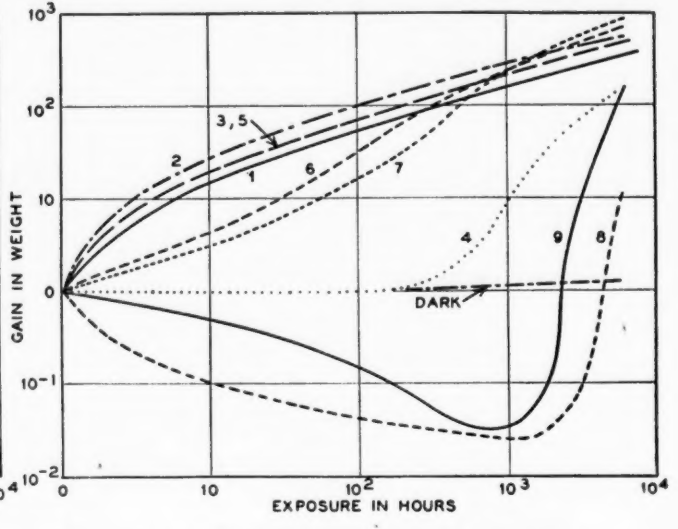


FIG. 9.—Results in Figure 8 Recalculated on Basis of Equal Weights of Rubber

increase in weight of the compound after irradiation in air by the light from a G.E. S_1 sun lamp, at 12 inches distance (ambient temperature 90–100° F) for a total of approximately 6000 hours.

	6. White wire insulation	7. White side wall	8. Tire tread	9. Reclaim insulation
	Parts by weight			
Crepe rubber	31.0	45.0	..	..
Smoked sheet	..	..	61.0	7.0
Reclaim (whole tire)	..	..	..	44.0
Sulfur	0.8	1.3	1.8	1.5
Zinc Oxide	21.0	11.0	3.0	1.4
Carbon black	..	..	30.0	..
Whiting	44.8	..	..	34.1
Titanox	..	20.0	..	..
Magnesium carbonate	..	3.5	..	..
Mineral rubber	..	..	..	10.0
Pine tar	..	1.8	..	..
Sunproof (wax)	..	1.3	..	1.1
Stearic acid	0.5	..	..	0.25
Laurex	1.2	1.3	..	..
Neozone-A	..	..	0.6	..
Agerite White	..	..	..	0.25
Flectol-H	0.8	..	..	..
Captax	..	..	0.6	..
Oxaf	..	0.3	..	..
Delac-P	..	0.3	..	..
Tuads	0.3	..	..	..
Altax	0.30	..	..	..
Thionex	..	..	..	0.14

Figure 10 shows the diffuse light reflectances of these compounds. By the addition of whiting or quartz alone, the light absorption (converse of reflection) in the assumed actinic range (4000 to 5000 Å.) is only slightly affected; in the white wire insulation and side wall it is greatly reduced. Total absorption may be assumed in the cases of the black samples 4, 5, 8, and 9, except for a small reflection by reason of the gloss of the surface.

Figure 8 shows the gains in weight as a function of exposure per unit area of compound exposed and Figure 9, the same results calculated on the basis of equal rubber content. Excluding for the moment compound 5 containing mineral rubber, the curves fall into three well-defined groups:

1. The filler has a refractive index approximately that of the rubber and therefore modifies but slightly its reflectance characteristics.
2. The total reflectance is markedly enhanced by fillers of high refractive index—*i.e.*, compounds filled with zinc oxide and titanium oxide.
3. Compounds containing carbon black where the total reflectance is greatly reduced.

In the first group a high initial rate of oxidation is quickly followed by a steady fall, which continues for several thousand hours. This fall in rate is doubtless a result of the increase in opacity of the oxidized surface which thus reduces the penetration of light, and the formation of the inelastic oxidized skin, which reduces the rate of sorption of gas. The type of filler included in this group does not affect the nature of the oxidation; but it does result in an increase in the amount of rubber broken down in a given time, due to greater absorption of light by scattering within the mass from the particles of filler,

and to easier access of air which is a consequence of the greater permeability (by actual measurement) to gases of the filled compounds.

In the second group the initial rate of oxidation is greatly reduced, a logical result of the opacity and the highly reflective properties imparted by the fillers of high refractive index (zinc and titanium oxides); the light activated oxidation is thus confined to a very thin film at the surface. As oxidation proceeds, however, some discoloration takes place at the surface, and the rate of weight increase actually exceeds that of the more transparent compounds. In the case of the white wire insulation, the end of the exposure period found the sheet embrittled throughout the entire thickness while the side wall compound was

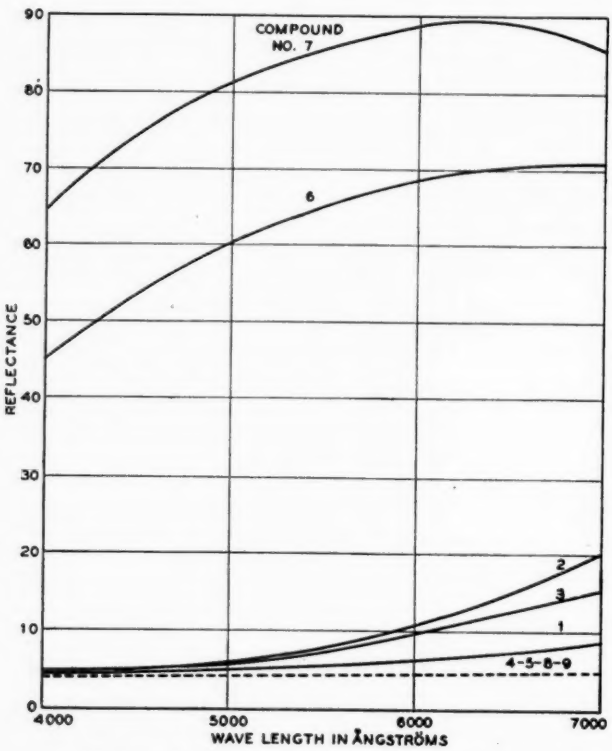


FIG. 10.—Spectral Reflectances of Compounds 1 to 9

in similar but somewhat better shape. Light penetration, however, had occurred only to a small fraction of the total depth as evidenced by the degree of discoloration in a cross section of the sheet. Yet the dark-exposed samples showed almost negligible increase in weight and little loss of physical properties. It is possible that peroxidic substances formed in the illuminated zone at the surface may migrate into the mass of the rubber and there catalyze its oxidation. Or perhaps the accelerated rate as compared with the unfilled rubber may be attributed to the zinc and titanium oxides which are well-known photosensitizers[11]. A "photosensitizer" is any substance capable of absorbing light and conveying the energy so absorbed to the reactants and, thus, of increasing

the efficiency of the photochemical process. It should be pointed out that in outdoor exposure the course of oxidation would be modified by the action of rain with the accompanying removal of soluble products. Discoloration would be reduced, permeability maintained, the rate of oxidation thus accentuated. In those compounds containing mineral fillers, loss of weight will ensue by "chalking".

In the third group opacity is conferred on the rubber by incorporation of carbon black which absorbs the light and thus protects the rubber beneath. (The rubber on the extreme outer surface of the sheet naturally cannot be protected by the carbon beneath it.) Oxidation of such a compound would be expected to be small, perhaps comparable to thermal oxidation; and, apart from the weight loss of compounds 8 and 9 due to volatile matter, this holds true for some time. But peroxidic substances in small quantity are formed in the very thin unprotected outer layer and in due course are possibly able to start the autoöxidation indicated by the curve of Figures 8 and 9.

The subsequent high rate of reaction in compound 4 may be a result of the higher temperature such a black compound attains under irradiation. The enormous increase in reaction rate of compounds 8 and 9 in the later stages cannot now be explained, but its occurrence was confirmed by a second similar experiment. The rates of thermal oxidation of the specimens at the end of the exposure period, except for those containing carbon black, were roughly in the order of their weight gains by the light-energized oxidation. The 24-hour bomb aging in oxygen at 60° C and 300 pounds per square inch gave the following increases in weight, calculated on the basis of equal weights of hydrocarbon [1 sq. dm. of rubber 0.025 inch (0.06 cm.) thick]:

Compound No.	1	2	3	4	5
Weight gain (mg.)	208	270	270	31	205
Compound No.	6	7	8	9	
Weight gain (mg.)	387	645	50	43	

The gain for the unexposed samples was around 10 mg.

That is, light exposure not only brings about an accelerated oxidation on its own account, but also accelerates thermal oxidation, which suggests their fundamental identity. A further example follows: sheets of compound 2 ($0.025 \times 2 \times 6$ inches) were light-exposed for progressively increasing periods and then subjected to bomb aging for 140 hours at 60° C and 300 pounds per square inch. The weight gains were:

Exposure (hrs.)	0	1	2	5	11	28	65	86
Gain in wt. (mg. per sq. dm.) due to:								
Light oxidation	0	8	14	20	30	54	96	116
Subsequent bomb-aging	38	42	45	46	47	53	66	74

In the preceding accounts of the light-activated oxidation of vulcanized rubber, there is little to suggest that any fundamental difference, except in degree, exists between the mechanisms of the thermal and of the light-activated oxidations, or that much can be done to control it to any great extent as long as the chemistry of the rubber molecule remains what it is.

Apart from some inhibition by antioxidants, the only practical means of present control is to shield the rubber from the light by an inert coating or incorporation of a suitable filler. From this aspect, fillers having little effect on the optical properties of the rubber save only to promote its deterioration. Fillers conferring a high degree of reflectance on the compound are efficacious

for a time but may lead ultimately to breakdown if present in insufficient amount to maintain the reflectance. By far the best of these is titanium oxide. Fillers which absorb the whole of actinic light and are finely divided enough to do this in a very thin layer are reasonably efficient; the best are carbon black and ferric oxide (Mapico). The usefulness of carbon black in protecting rubber from light is well known, and as little as 2.5 per cent confers appreciable protection. Ferric oxide in additions of 5 per cent by weight and over is equally as efficient as carbon black, as shown by experiment similar to that depicted in Figure 9. It is futile, however, to attempt to confer opacity by an opaque material which in itself is oxidizable, such as asphalt—for example, compound 5 (Figure 9). Nor (from other experiments) do dyes seem to be efficacious to any degree. In these cases the absorbed light probably is not degraded as heat but its energy is passed on in some manner to the rubber; that is, the dye acts as a photosensitizer in greater or lesser degree. This is a frequent property of dyes.

EFFECT OF OZONE

The multiple cracking which stretched rubber experiences on outdoor exposure is due, not to the effects of light, as is commonly supposed, but to the ozone contained in the atmosphere[12]. Previous workers[13] arrived at the same conclusion, but its importance in weathering was evidently not fully realized; for the past ten years no publication known to the authors has discussed this feature, although devices for accelerated weathering relying solely on high-energy light sources and water treatment have been actively employed. Perhaps it is hardly to be expected that an ingredient present in such minute concentration could effect changes in rubber commensurate with those resulting from a large energy source such as sunlight. In consequence widespread confusion of ideas among rubber technologists exists as to processes in the weathering of rubber. Proof that cracking is due to ozone and not to light follows:

1. Light and air in the absence of ozone do not cause cracking in moderately stretched rubber (up to 50 per cent elongation) and at higher elongations only when the entire rubber mass is greatly deteriorated; in the latter case the manner of rupture is entirely different from that popularly designated "light cracking" (Figure 11).
2. Stretched rubber cracks out-of-doors just as rapidly at night as in the daytime, and in the daytime just as quickly in the shade as in the open (or more quickly).
3. Ozone generated in the laboratory at the same concentration as in atmospheric air duplicates in every detail the cracking of rubber out-of-doors in the shade.
4. Tests by the authors have demonstrated that no other component of the atmosphere can possibly crack rubber within the same time or in the same manner.

Ozone, even in high concentration (1–5 per cent), has no apparent effect on relaxed vulcanized rubber. On stretching the rubber ever so slightly, however (even 2 per cent is sufficient), the rubber is rapidly attacked locally, presumably at zones of higher energy brought about by some rearrangement of molecular forces as a result of stretching. In air of high ozone content the rubber is entirely disrupted at these points in a few minutes. In dilute ozone the disruption takes longer, is less in degree, and appears as cracks or cuts in

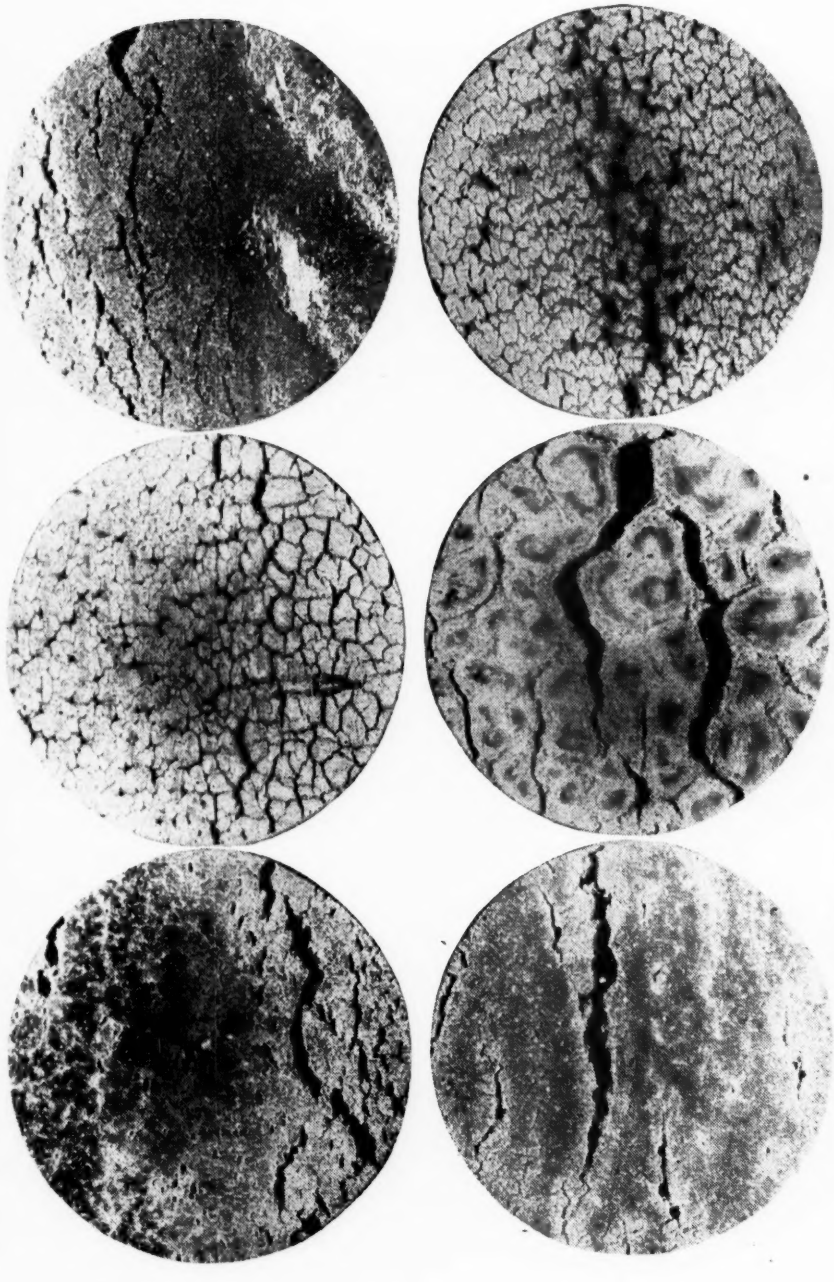
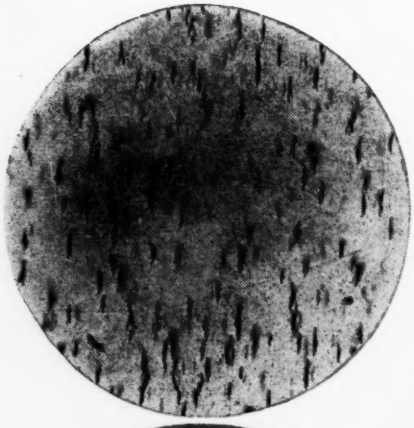
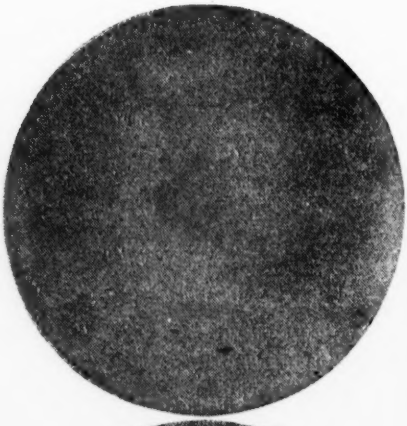
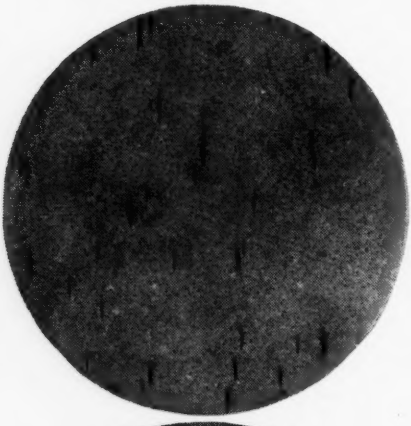
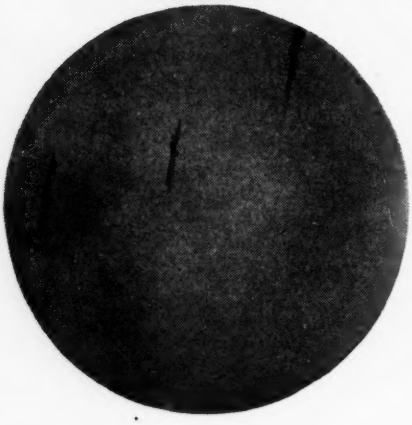


FIG. 11.—Types of Cracking of Stretched Rubber Compounds Due to Light, Oxygen, and Moisture (×7)









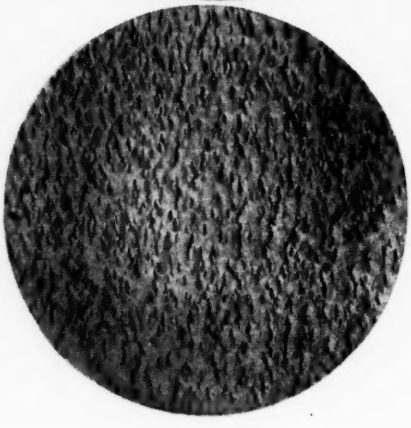


FIG. 12.—Effect of Degree of Elongation on Early Stages of Ozone Cracking

the surface at right angles to the direction of elongation; the rubber in the intervening spaces is unaltered. At low elongations, say up to 10 per cent, the number of cuts is a few per centimeter, depending on the type of compound, and they are deep. As elongation increases, the number of reactive zones increases; the cuts, therefore, become more frequent but less deep until at 100 per cent elongation the cuts are myriad but very shallow. The surface takes on a

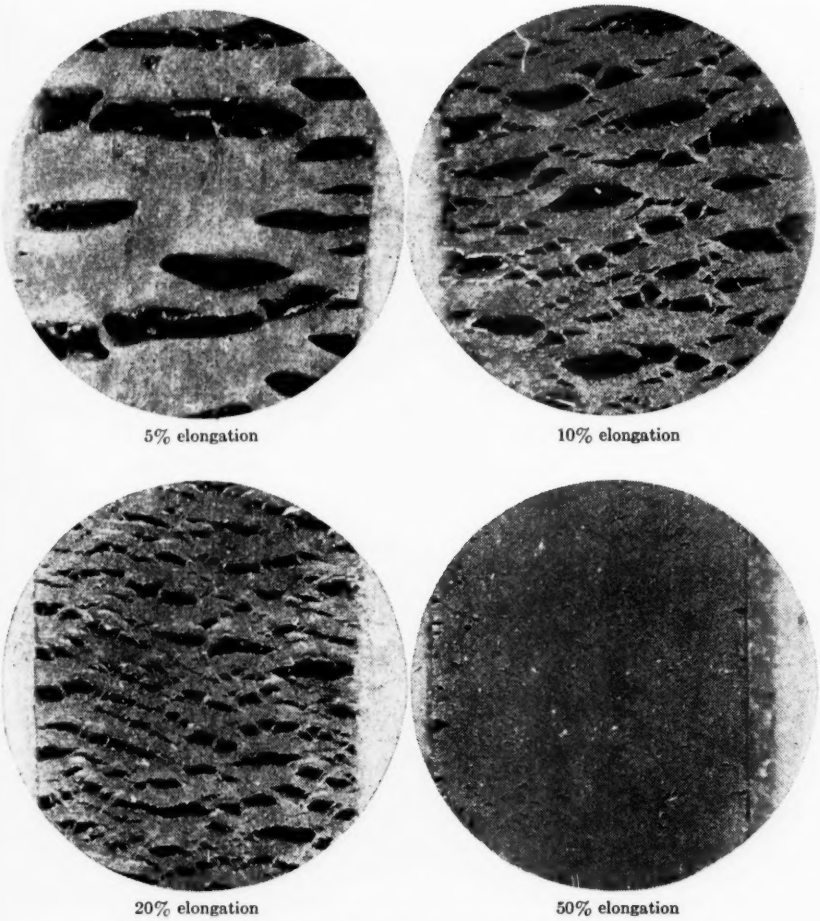


FIG. 13.—Effect of Degree of Elongation on Later Stages of Ozone Cracking
0.075-inch sheet of compound 4, reflected light (×7)

roughened appearance, but the characteristic nature of the cuts is evident when observed at a slight magnification. Figure 12 shows the early stages of cracking of a sheet 0.025 inch thick of base compound 1, observed under the microscope (×7) by transmitted light. Figure 13 shows a sheet 0.075 inch thick of the same compound plus 5 per cent carbon black (for easier viewing) at a later stage of cracking (×7).

100% elongation
50% elongation
30% elongation
FIG. 12.—Effect of Degree of Elongation on Early Stages of Ozone Cracking

Usually it is stated that there is an optimum degree of stretch for maximum cracking effect, generally at 10 to 20 per cent, depending on the compound. This is a moot point. The degree of cracking does not lend itself easily to measurement and its extent is a matter of subjective impression, depending on the point of view of the observer. The uncertainty arises from the changing character of the cracks with their number and with the physical properties of the compound

OZONE CONCENTRATION IN AIR

The presence of ozone in the atmosphere has been known for a hundred years, but estimates as to its concentration vary widely. As a result of work in recent years, however, the situation is now fairly clear. Ozone is formed from oxygen by photochemical action of the short-wave ultraviolet radiation in the stratosphere. It is not formed in the atmosphere near the earth's surface because light of the necessary wave length is not present at or near the

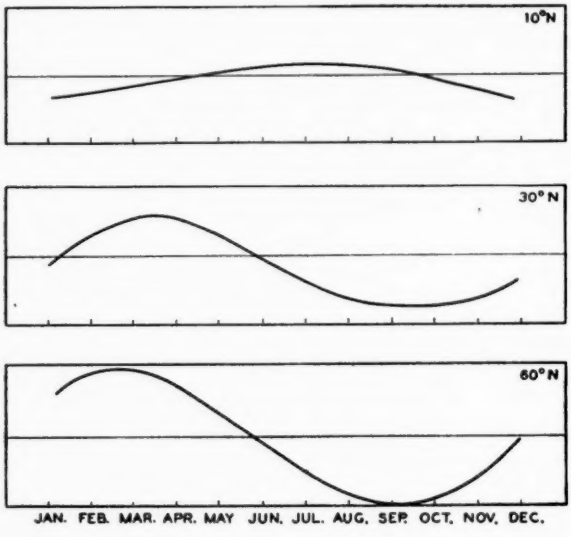


FIG. 14.—Seasonal Variation of Total Ozone in Atmosphere at Different Latitudes[18].

earth's surface, but has been totally absorbed in its passage through the upper atmosphere. The ozone at the earth's surface is brought down from the upper atmosphere by convection currents. Its life here is short. First, sunlight gradually breaks it down again into oxygen. This may seem anomalous, but oxygen absorbs the short ultraviolet light and the oxygen atoms from the resulting dissociation recombine to form ozone, while ozone absorbs longer wave lengths to decompose back into oxygen. The resulting concentration depends on the equilibrium between the two processes. Second, ozone is a powerful oxidizing agent and is rapidly used up by sulfur dioxide, smoke, and other organic particles suspended in the air and by organic matter on the earth's surface. In fact, ozone is said to be absent or very low in concentration in thickly populated industrial areas. Third, ozone is decomposed catalytically in contact with a variety of surfaces. The concentration of ozone in any locality is, therefore, a variable result of meteorological and topographical conditions.

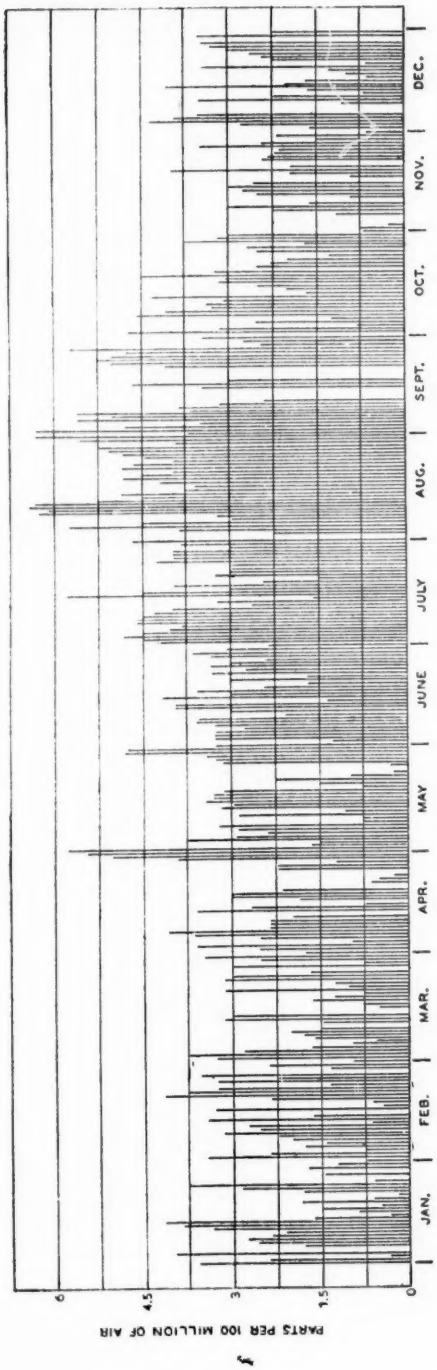


FIG. 15.—Day-by-Day Content of Ozone in Atmosphere at Murray Hill, N. J., from January 1 to December 31, 1944

The total amount of ozone in the whole atmosphere is fairly constant. It can be determined spectroscopically by comparison of sunlight absorption at two wave lengths, one in the region of absorption by ozone, the other at a region of transparency. The total in the atmosphere would make a layer of pure ozone about 1 to 4 mm. thick. It varies throughout the year, reaches a maximum in the spring, and is at a minimum in the fall. The total amount and the variation are least at the equator and increase toward the poles (Figure 14).

Information on the concentration at the earth's surface is meager although probably millions of measurements have been made in the past fifty years with values varying from zero to a few parts per million. A few spectroscopic determinations using light sources a mile or two distant give values of a few parts per hundred million, but such measurements are difficult. For general usage chemical methods must be used, the classical one being based on liberation of iodine from potassium iodide. A recent modification in which the ozone is absorbed by a fine spray of potassium iodide solution, following a suggestion by Paneth and Edgar[14], has been used in daily measurements in these laboratories for the past two years. These results (Figure 15) show the daily (8:30 A.M. to 5:30 P.M.) content of the outdoor atmosphere at Murray Hill, N. J. (a rural location 20 miles due west of New York) from January 1 to December 31, 1944.

The most obvious feature of the record is the variation in the ozone content. A high ozone content one day may be followed by none the next day or *vice versa*. A comparison of these values with current meteorological conditions points to a connection with the velocity and direction of the wind. A calm day usually shows low ozone content and a windy day, high values. This is generally the case when the wind is from a predominantly westerly direction. Wind from an easterly direction is usually associated with low ozone. Easterly winds pass over the thickly populated and industrial areas of New Jersey befor reaching this location, which may account for their lower ozone content. However, even the total ozone in the atmosphere above any particular location fluctuates somewhat from day to day; total ozone content is higher during cyclonic depression and lower during anticyclonic highs. A rigid connection with wind velocity is not to be expected, since replenishment of ozone depends on upper air disturbances which may not parallel wind at the earth's surface. It is, however, a useful generalization for practical purposes.

In Figure 15 there is no indication of the annual spring peak or fall trough of total ozone content noted previously, but the high ozone incidence appears during late summer. Dependence on local conditions apparently cancels this variation. Tests have also shown that, with weather conditions the same, there is no difference between day and night ozone content. Like other weathering factors, ozone cracking out-of-doors must be a variable factor depending on meteorological conditions and on location.

Outdoor air containing 3 or 4 volumes of ozone per 10^8 causes cracks in stretched rubber which are readily seen under fifty-fold magnification within an hour or so; in 12 hours a hand magnifier will suffice, and after 24 hours, the cracks will be visible to the naked eye. One observer[15] considers a stretched rubber band to be the most sensitive test known for the detection of ozone.

RUBBER DESTRUCTION BY OZONE

The factors involved in the destruction of rubber by ozone have been studied here over the range of concentrations (0–500 parts per 10^8) expected in nature

or feasible for accelerated testing. Many methods of generating ozone in small controllable amounts have been tried. Maintenance of a uniform concentration was found difficult with electrical methods, sudden variations occurring with no apparent reason. Moreover, when used in air, nitrogen oxides are also produced although their presence does not seem to be a disadvantage. The method finally adopted is the simple one of enclosing a small mercury-vapor lamp (in quartz) in a large flask through which air is passed. The ultraviolet light coming from the lamp has enough short-wave energy to generate considerable amounts of ozone from air passing over it. The amount of ultraviolet light can be controlled to a considerable extent by a Pyrex sleeve slipped over the quartz tube; adjustment of the sleeve allows a wide variation in the amount of ozone-generating ultraviolet light passing through to the enclosed air. The issuing ozonized air can be further diluted with more air to bring the mixture to any desired concentration. As little as 1 part in 10^8 is readily maintained. Figure 16 is a schematic diagram of the apparatus. Rubber stoppers

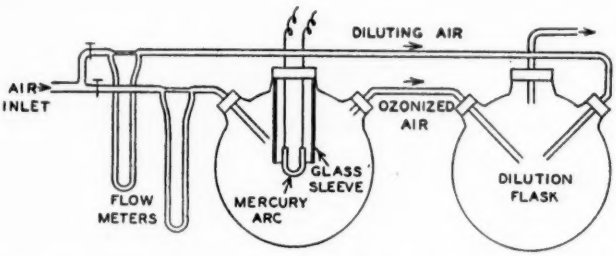


FIG. 16.—Assembly for Furnishing Ozonized Air at Very Low Concentrations

may be used if a few pieces of wax are introduced into the flasks and, after assembly, are melted and allowed to coat the exposed rubber. Connections in the tubing may be made with heavy rubber pressure tubing which will last a long time before cracking through. Less convenient but more durable is flexible plastic tubing. A well-used burner gives a more constant output than a new one. Instead of the quartz mercury arc a General Electric Germicidal lamp or a Westinghouse Sterilamp may be employed, but the lamp must be encased in a wide glass tube. The production of ozone from these lamps is considerably less than from the quartz arc but will be found ample for laboratory purposes. Since mercury arcs show substantial changes in output with temperature and voltage, it is advisable for uniform ozone production to maintain the incoming air at a constant temperature and to use a voltage regulator. It is well to dry the air over calcium chloride to avoid variations in humidity, although it has not been found that humidity affects ozone concentration. (The analysis of the issuing ozonized air is dealt with elsewhere.) The reaction vessel in which the rubber tests are conducted is preferably glass. Ozone is rapidly decomposed at metal surfaces, so metal vessels must first be coated with wax. Wooden supports for the rubber specimens must also be waxed. In fact, it is a wise precaution to wax everything with which the ozonized air comes in contact (other than the specimens) for ozone at atmospheric concentrations is very unstable. Specimens may conveniently be studied as strips 0.25 inch wide and 0.075 inch thick, stapled at progressively increasing elongations to a waxed board, or as loops whose ends are thrust into holes in the board. Temperature effects were studied by passing the ozonized air through a flask

immersed in acetone cooled by dry ice and thence to a reaction vessel, consisting of a long glass tube wound with Nichrome wire of progressively closer spacing, through which an electric current is passed. Thus a temperature gradient is maintained enabling simultaneous exposure of specimens over a range of temperatures. Up to about 160° F little or no decomposition of the ozone ensued as a result of temperature effects. By such methods, the following observations were made:

Elongation of Rubber.—Degree of elongation has already been mentioned (Figures 12 and 13). The lower the elongation, the fewer but deeper and more disruptive are the cracks. This is probably a result of localization of the residual stress in the clefts which generates more points of attack. The practical consequences of this unfortunate characteristic are obvious in such applications as wire insulation where one deep crack is worse than many shallow ones.

Concentration.—Over the range of concentrations expected in weathering and with the difficulties of appraisal, the effect of concentration does not seem to be a reciprocal of time. That is, a low concentration acting for a long time has a greater effect than a higher concentration acting for a proportionately shorter time. The cracks at lower concentration seem fewer and deeper.

Time.—The increase in cracking with time does not seem to be proportional to time, *i.e.*, double the time has less than double the effect. It should be remembered that, as cracks appear, the stress decreases.

Temperature.—Ozone at concentrations similar to those present in the atmosphere cracks rubber at temperatures as low as −40° F, although the onset is somewhat delayed and the cracks are few in number. As the temperature is increased, the cracks at any given elongation increase progressively in number but decrease in size. A series of specimens at a fixed elongation but progressively increasing temperatures present a similar picture to that of a series exposed at fixed temperature but having progressively increasing elongations (Figure 17). For example, rubber stretched 20 per cent at 140° F presents the same appearance as rubber stretched 100 per cent at room temperature. This is not caused by change in stress due to heating (which is negligible), but is a pure temperature effect. In short, increasing the temperature produces the same effect as increasing the strain, the increased thermal agitation of the rubber molecules presumably setting up more reactive zones. By this reasoning, even relaxed rubber should show points of attack by ozone if the temperature is raised sufficiently; trial indicates that this is true, for a strip of rubber exposed in a relaxed state to an atmosphere high in ozone (about 1 per cent) at 200° F for half an hour showed, under magnification, small characteristic ozone cracks. However, it is possible that the cracks may have originated at points of strain which are set up around foreign particles or other inequalities by the increase in temperature. Above 0° F, as far as can be judged, the onset of attack in stretched rubber is the same.

Humidity.—Change in humidity has no discernible effect on any phase of ozone cracking.

Wind Velocity.—In outdoor exposure it was thought that the rate at which the air swept over the surface of the rubber might have some effect on the rate at which cracks appeared. Rubber specimens at different elongations were mounted in a series of interconnecting glass tubes of progressively increasing diameter. Outdoor air was aspirated through this device to secure a current over the specimens at speeds from 1 to 40 miles per hour. Although a perceptible increase in the degree of cracking was seen at the high velocities, it is unimportant. This is an indication that differences in wind velocity as such

Fig. 17.—Effect of Temperature on Early Stages of Ozone Cracking of Uniformly Stretched (20%) Rubber 0.025-inch sheet of compound 1, transmitted light (×7)

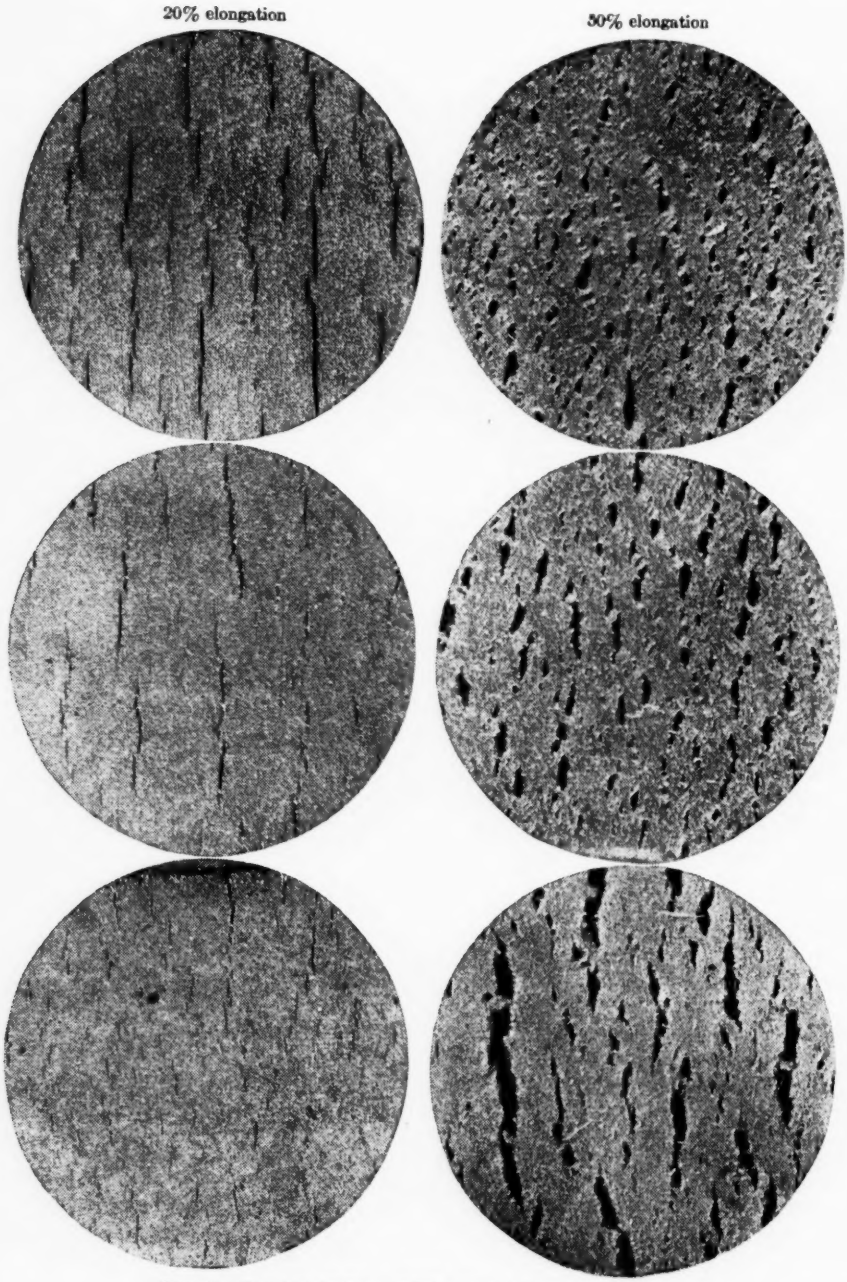


FIG. 18.—Effect of Addition of Filler (Whiting) on Ozone Cracking (×7)

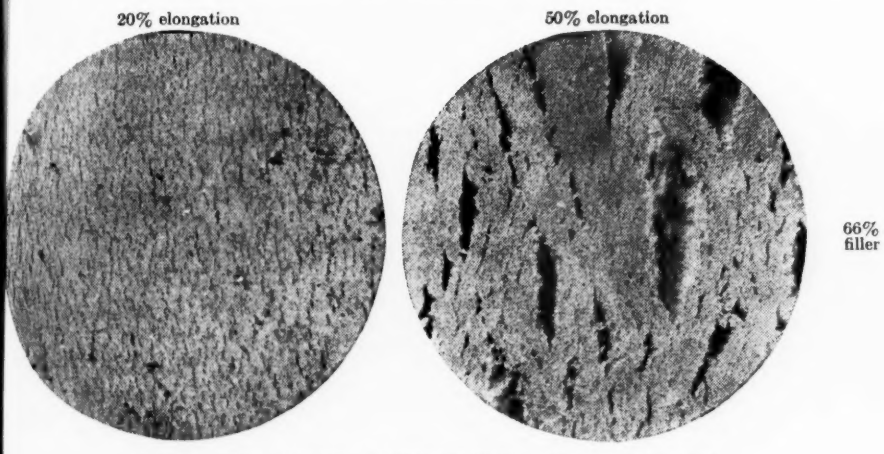


FIG. 18.—Effect of Addition of Filler (Whiting) on Ozone Cracking (×7)

are not of great importance. Incidentally, compressor air containing no ozone was also used in this device to confirm that cracking was due to ozone and not to a high-velocity stream of oxygen. Samples of rubber exposed continually to such a stream for 100 hours and subsequently for 24 hours, while illuminated by a quartz mercury arc, did not show the slightest sign of cracking.

Cure.—There appears to be little connection between rate or degree of cracking and the state of cure within the usual limits. However, when improper cure results in a dense, tenacious bloom of sulfur, this may act as a barrier to ozone and delay creacking for a time.

Grain.—The direction of grain in a rubber sheet has no effect on the direction of the cracking, which is always at right angles to the direction of the stress.

Time between Stretching and Exposure.—When specimens are stretched and allowed to stand for some time before exposure, the resulting decay of stress in those compounds having a high degree of permanent set is manifest in the type of cracking which ensues. Where the permanent set is large, as in ozone-resisting-power cable stocks, cracking is considerably reduced.

Fillers.—In their influence on ozone cracking, all the reinforcing fillers act substantially according to one plan, although to different degrees. Observations were made on carbon black, clay, whiting, crushed quartz, zinc oxide, titanium oxide, and magnesium carbonate. At any given degree of stretch, addition of increasing amounts of filler produces the same effect as increasing the degree of stretching or the temperature of the unfilled rubber. That is, the number of cracks becomes greater, but their size and depth are less. At small degrees of stretch (up to 10 or 15 per cent), the net effect of increase of filler is beneficial, since the smaller cracks are less disruptive. At higher degrees of stretching, however, the high stress on the rubber between the particles of filler results in opening up enough of the cracks to give a picture of increasing disruption (Figure 18). The efficacy of the fillers in this regard was in the order: zinc oxide, titanium oxide, magnesium carbonate, clay, whiting, quartz. The picture of carbon black (Figure 19) does not seem at first to fit in this scheme since, at low degrees of stretching, increase in filler results in progressively fewer but deeper cracks. It is probable that, even at low stretching, due to the high stiffness, the rubber bonding the carbon particles is in much the

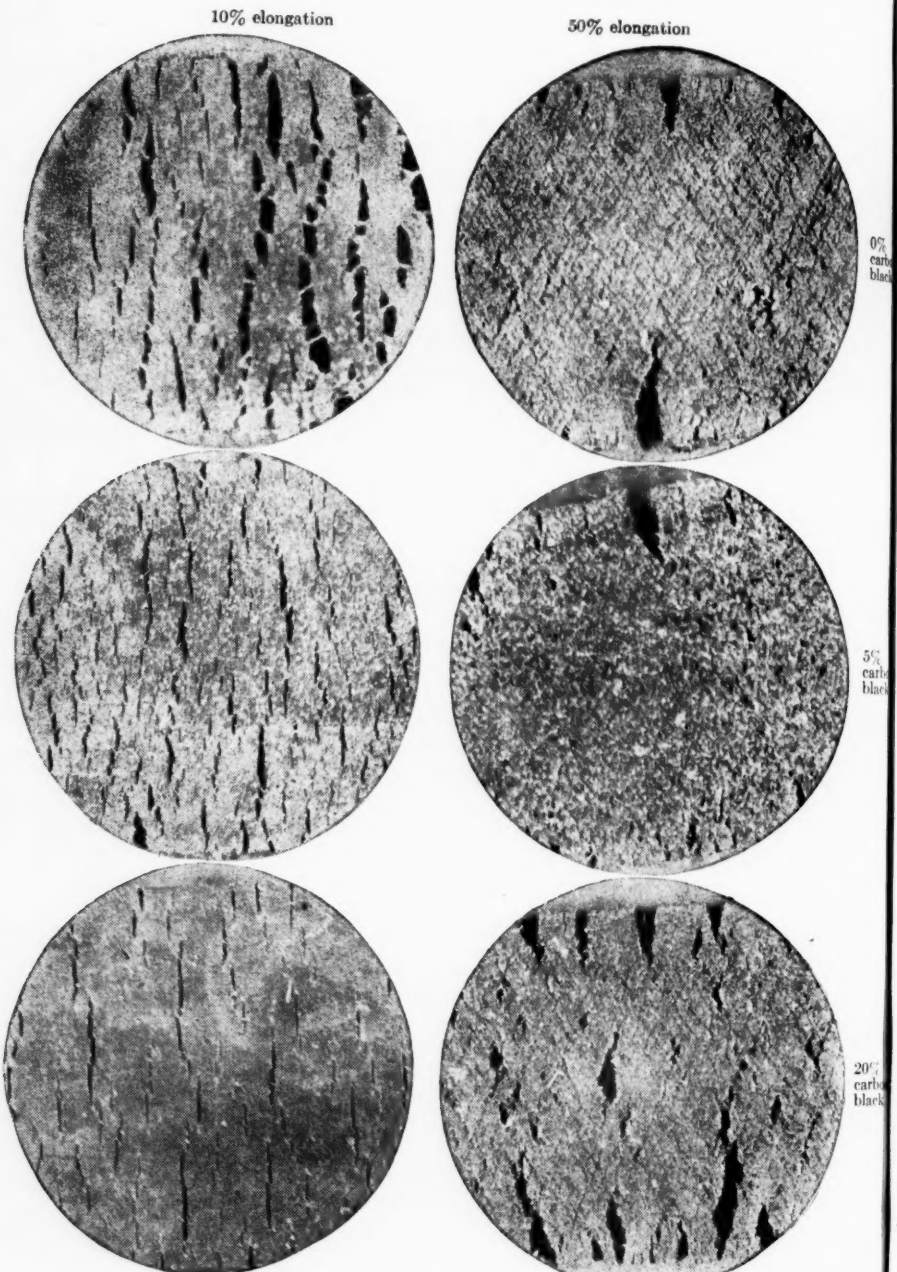


FIG. 19.—Effect of Addition of Reinforcing Carbon Black on Ozone Cracking (×7)

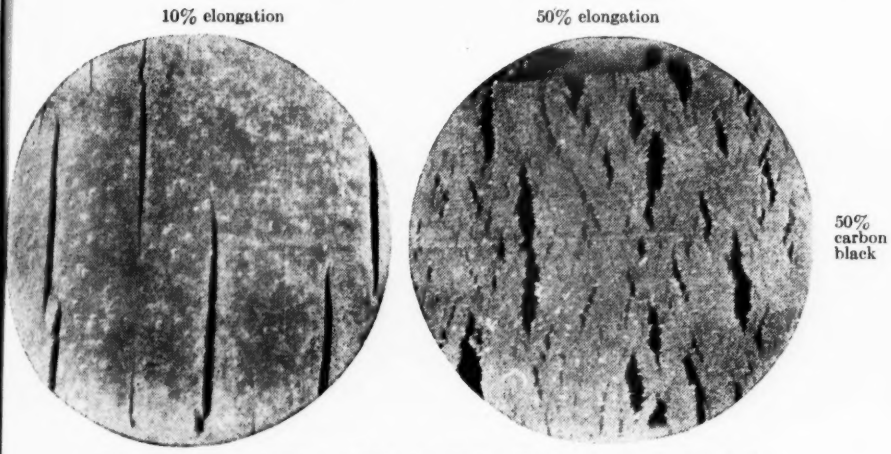


FIG. 19.—Effect of Addition of Reinforcing Carbon Black on Ozone Cracking (×7)

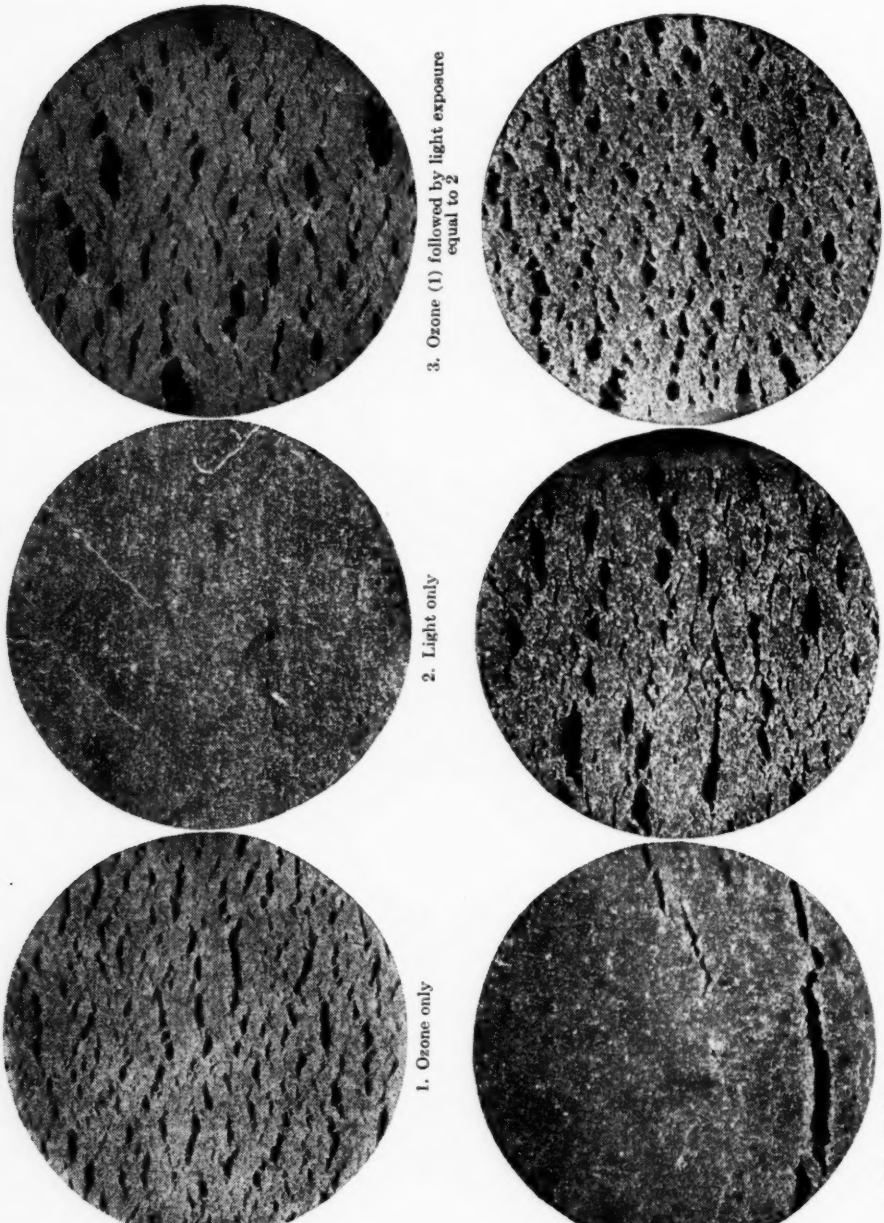
same state of stress as the higher stretches of the other fillers, and failure occurs at the relatively weaker locations. Carbon black, therefore, should probably head the list in the above rating.

Light.—It is improbable that light has any effect on the basic reaction between rubber and ozone; however, the accompanying photoenergized oxidation of the rubber which occurs during weathering does modify the overall result in many cases, and is a consequence of the change in physical properties of the rubber. In the case of rubber adequately protected from light by enough carbon black or ferric oxide, the behavior is almost identical in light and in darkness. With rubber compounds insufficiently protected from light, the inelastic surface skin and the loss of tensile strength do affect the picture, depending on whether the light effect preponderates and on the order in which these two changes take place in the rubber. If such a compound is exposed in a stretched condition to light in the absence of ozone until a surface skin is formed and, subsequently, to air containing ozone, the skin acts as a barrier protecting the underlying rubber, and cracking is prevented for some time, provided the skin is not broken by flexing. Ultimately, however (particularly if subjected to rain), temperature changes produce a few cracks in the inelastic skin, ozone gains access to the underlying rubber, and a few deep splits result. The overall appearance is unlike typical ozone cracking. If the rubber, on the other hand, is first exposed to an ozone-containing atmosphere in the dark until typical ozone cracking appears and then is exposed to light and air in the absence of ozone, the resulting formation of surface skin coupled with the deterioration of the rubber tears apart the existing ozone cracks and produces aggravated ozone cracking. Simultaneous exposure to light and to an ozone-containing atmosphere gives a result somewhere between these two extremes, which depends on the balance between the light and ozone effects and their chronological order (Figure 20).

Here lies the explanation of the variance in the results of aging of a given compound in different localities and in different seasons.

PROTECTION OF RUBBER FROM OZONE

The susceptibility of rubber to attack by ozone is a consequence of its unsaturation, ozone adding on at the double bonds to form ozonides. If the



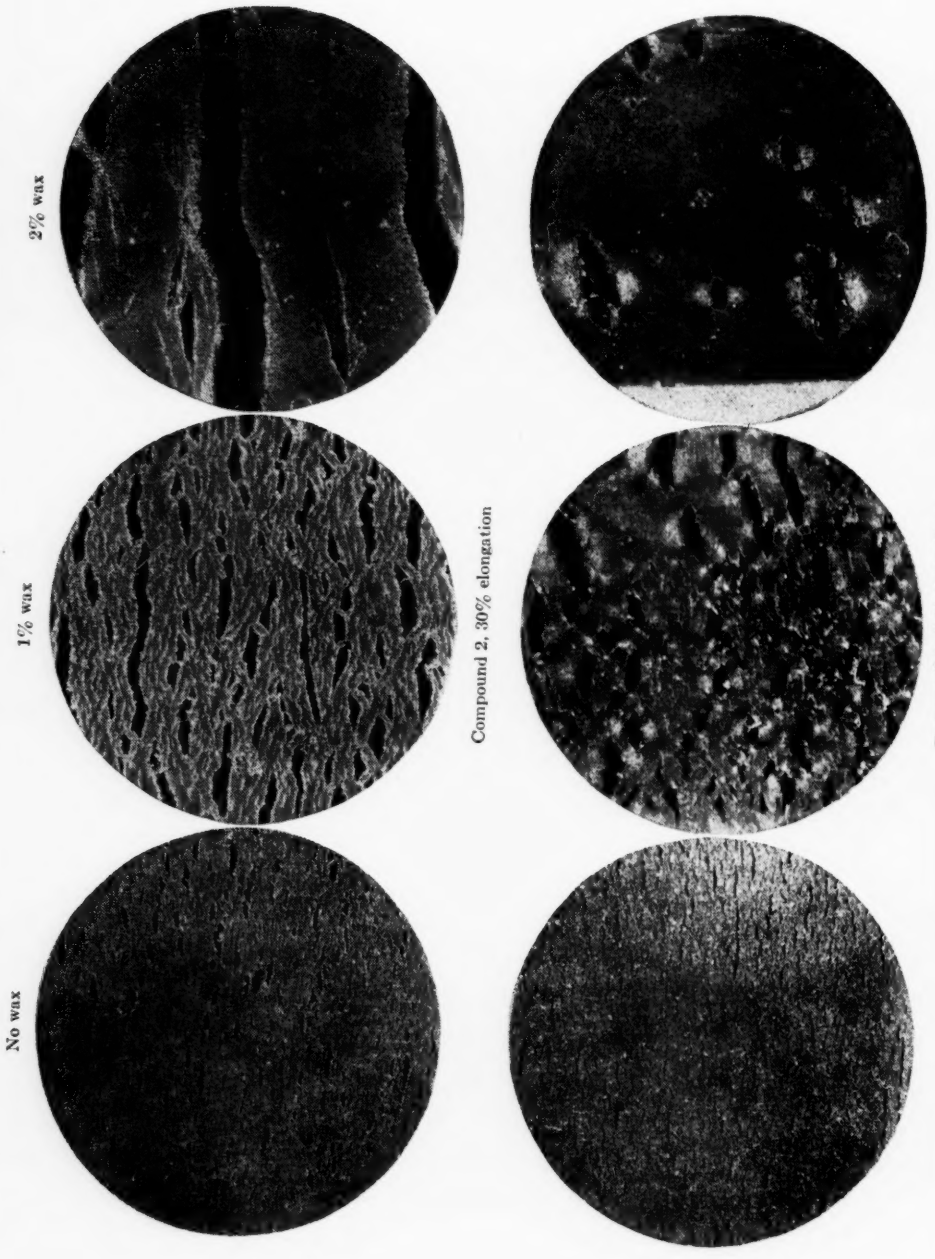
1. Ozone only
2. Light only
3. Ozone (1) followed by light exposure equal to 2
4. Light (2) followed by ozone exposure equal to 1
5. Outdoor full summer sunlight
6. Outdoor partial shade

unsaturation is removed, the susceptibility disappears. A surface layer of saturated material which protects the underlying rubber from attack by ozone can be formed in several ways—*e.g.*, exposure to light and air, to hydrogen peroxide, bromine, nitrogen peroxide, and even bomb aging. Unfortunately, this layer is now no longer rubber but a brittle substance which does not bear flexure, cracks in due course without flexure, and thus nullifies the protection. Addition to the rubber of more highly unsaturated substances with the idea of competing with the rubber for the available ozone has proved useless, as demonstrated by incorporation of highly unsaturated drying oils and various chemical compounds such as sorbic acid, $CH_3CH{=}CH{-}CH{=}CHCOOH$. As might be expected from the nature of the ozone reaction, antioxidants are also without protective effect.

Bearing in mind that ozone decomposes at surfaces, the idea of covering the rubber with various fine powders to simulate dusty bloom was tried without effect. Any material which exudes from a rubber compound to form a continuous surface layer protects the rubber from ozone for a time; the only substances which do this for a commercially useful period are certain pyrrole compounds[16] and waxes which, if added in sufficient quantity during compounding, do protect rubber from the effects of ozone in the atmosphere. The wax seems to act in some way as a protective varnish, since it is ineffective until it has bloomed out to the required degree, and since most waxes which do not bloom but remain in solution in the rubber, as do the vegetable waxes, are useless. Although the protection conferred by wax seems to be associated with a bloomed-out film of wax, this simple impervious-barrier theory has the grave defect that the wax is not a barrier to other gases. Measurements of the rate of absorption of gases by waxed and unwaxed compounds show little difference; what difference there is between them is just as great in those waxes which have no protective effect against ozone. Hydrocarbon waxes seem to be the only useful ones. A proprietary wax of proved efficiency was used in these experiments. However, there are many pitfalls in the utilization of waxes for this purpose. For a given addition of wax, there is a concentration of ozone above which the wax is no longer effective; *e.g.*, for a gum rubber stretched by 20 per cent an addition of 1 per cent of a certain wax does not protect from a concentration of ozone higher than about 50 parts per 100 million of air, 2 per cent from 150 parts, and 4 per cent from 500 parts. These concentrations become less with increase in elongation and differ with the type of compound.

The degree of stretching at which the wax becomes ineffective is probably due to ruptures in the wax film; the higher the wax concentration, the higher the stretching necessary for failure. Moreover, when failure does occur, it is very disruptive, and the cracks are few but deep and wide. Obviously, too little wax is worse than none at all, since this brings the degree of stretching necessary for failure down to low limits. Figure 21 shows the result of exposure to dilute ozone (10 parts per 10^8) of rubber compounded with insufficient amounts of wax.

If a compound protected from ozone by wax is stretched to the point where the wax film breaks and is no longer effective and is then stored in the absence of ozone for some time, the wax protection is renewed as a result of further blooming of the wax to form a new and continuous film on the surface. Or if the surface of the stretched rubber is heated to melt the wax, continuity of the film is restored and the protection is renewed. On storage of rubber compounds containing protective waxes, the wax steadily blooms out. For sheets of a given thickness, it has been found that the fraction of the total wax content


2% wax
1% wax
No wax
Compound 2, 30% elongation
Compound 4, 30% elongation

Compound 4, 50% elongation

FIG. 21.—Effect of Insufficient Wax Addition on Ozone Cracking (×7)

which appears on the surface is the same regardless of the amount added, at any rate up to an original wax content of 10 per cent of the rubber; this is an indication that the wax is not in true solution but dispersed in the rubber in the manner of a plasticizer. The rate of blooming depends largely on the surface area of the goods and the loss, therefore, increases with increasing thinness. Goods stored for a year or so before usage, therefore, may prove to have partially or entirely lost the protective benefits of the wax additions. If put into use in midsummer, however, direct sunshine may raise the temperature of the goods to such a point that the wax is reabsorbed and protection restored. This is particularly true of black compounds which attain relatively high temperatures in bright sunlight. With the waxes in general use, absorption begins around 120° F.

Temperature has a profound effect on the efficacy of the waxes now in general use. Low temperatures (around 0° F and below) cause the film to crack, and scattered ozone splits then appear in stretched rubber. As the temperature is raised, protection is fully restored at about 20° F, and continues until temperatures of 100° to 120° F, are reached (depending on the particular wax), when protection disappears as a result of reabsorption of the wax into the rubber mass. The temperature at which this occurs increases somewhat with increase in the melting point of the wax, but does not run concurrently with it. Even waxes with melting points as high as 180° F lose their effectiveness around 120°. The temperature at which failure occurs increases slightly with increase in the wax content of the rubber, but even 10 per cent of wax brings about a rise of only about 10° F. The behavior of waxed compounds in midsummer or in tropical climates is, therefore, affected by the length of time during which the temperature of the rubber exceeds 110–120° F. Short periods may be beneficial by maintaining the wax content of the rubber through redispersal of the wax bloom as noted above.

Mineral loadings, by absorbing part of the wax, tend to reduce blooming and, therefore, the efficacy of the wax (Figure 22). Higher proportions of wax are called for in such cases. Softeners such as asphalt which can dissolve the wax prevent blooming and render the addition of wax in normal amounts almost useless. Ten per cent of mineral rubber almost nullifies the effect of as much as 3 per cent wax. Surface applications of wax to an otherwise unwaxed compound offer some temporary protection, but in the end, as the wax film is disrupted or is absorbed, are worse than useless, since the type of crack becomes that characteristic of low wax content—*e.g.*, few but deep and disruptive.

No wax addition prevents ozone cracking of rubber dynamically flexed. Repeated stretching obviously tends to break up the wax film. As in the case of static flexure with insufficient wax for full protection, the type of cracking produced is scattered, deep, and disruptive. For articles to be used under dynamic flexure, then, wax is actually injurious.

It might be thought that softening by addition of petrolatum, for example, would render the wax film more flexible and hinder its rupture on stretching. However, addition of petrolatum definitely reduces the efficiency of wax as a protection from ozone cracking. Petrolatum itself, and mineral oils incidentally, as ozone protectors belong in the "worse than useless" category since they lead to the deep type of cracking. Rubber goods containing wax, then, are more susceptible in outdoor exposure to change in conditions of weather and mechanical handling than are unwaxed compounds. However, such vagaries as are encountered find a ready explanation in terms of the factors outlined in this paper.

FIG. 22.—Effect of Filler on Protection of Rubber (30% Elongation) from Ozone by Wax (×7)

WEATHERING OF SYNTHETIC RUBBERS

Buna-S.—The fundamental structural relation between GR-S and natural rubber suggests that the physical results of the chemical changes involved in weathering should be similar. This is true with certain important modifications. As might be expected from its well known lower rate of thermal oxidation, GR-S is less susceptible to light-energized oxidation than is natural rubber. Of several samples measured, the GR-S rate varied from one-quarter to one-half that of natural rubber, using the following pure-gum GR-S formula, which is similar to natural rubber compound 1: GR-S 100, sulfur 2, zinc oxide 5, stearic acid 2, Akroflex-C 1, 2MT 2, and 808 0.5 part.

Figure 23 is a plot of gaseous oxygen absorbed by a representative sample

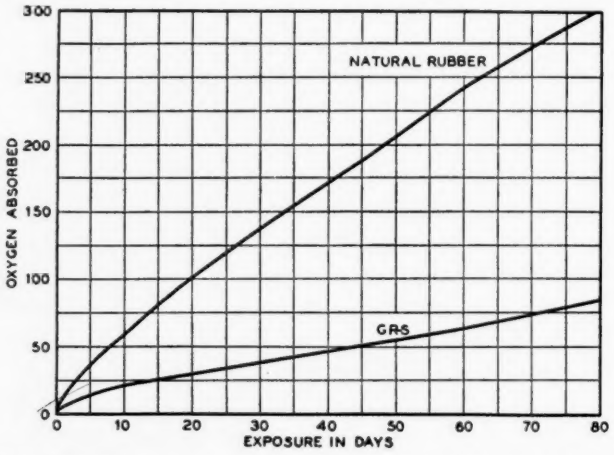


FIG. 23.—Relative Rates of Oxidation during Exposure to Light and Air of Gum Compounds of Natural Rubber and GR-S

of the GR-S compound in sheet form, compared with a similar sheet of natural-rubber compound 1. Exposure was by S_4 sun lamp. On the basis of Farmer's findings[8], the decreased susceptibility to oxidation would be expected from the absence in GR-S of the activating methyl group in the alpha position to the double bonds.

Most commercial samples of GR-S turn black on the surface as a result of light-energized oxidation. This is not a property of the hydrocarbon, but arises from antioxidants used during manufacture. Apart from this, the gross behavior of GR-S during exposure to light and air differs from that of natural rubber only in degree, and the conclusions drawn from natural rubber are applicable here. The effect of ozone (in atmospheric concentration) is also similar to that on natural rubber, but has some important differences. As might be expected from the lower modulus, the cracking pattern of GR-S at a given elongation is similar to that of natural rubber at a somewhat lower elongation. The degree of damage is less than in natural rubber in the initial stages, but in later stages is more disruptive. Complete rupture often ensues at elongations over 50 per cent, a probable result of the low tear resistance. Cracking does not occur below −20° F, and the change in size and number of cracks with temperature is much less pronounced in the case of GR-S (Figure 24). The overall aspect is one of greater susceptibility to ozone damage.

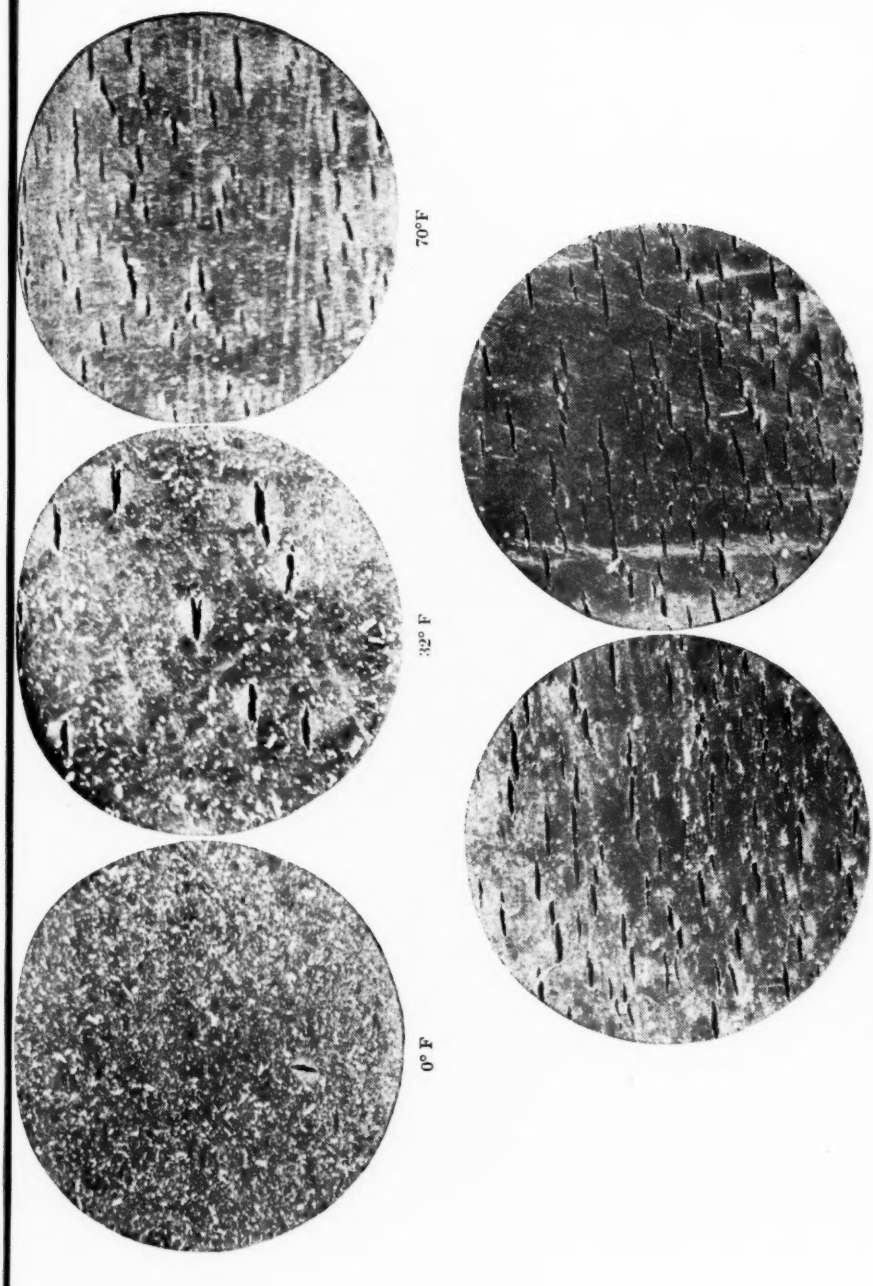


FIG. 24.—Effect of Temperature on Cracking of a GR-S Gum Compound (20% Elongation) by Ozone (×7)

Addition of protective waxes, however, changes the picture entirely, since these waxes prove more efficient in GR-S than in natural rubber, both as to concentration required and length of time over which they maintain their effectiveness. The rate of blooming is lower than in rubber by about 40 per cent (in the 0.075-inch sheets on which the determination was made), but this cannot account for the increased efficiency, which is at least 100 per cent in the case of gum compounds. The reason probably lies in the nature of the bloomed film, which exudes in a much more finely crystalline form than is the case with natural rubber. The wax also retains its effectiveness to a higher temperature than with natural rubber, failure occurring at about 120° F, compared with 110° for natural. Wax in GR-S is, however, just as useless (or worse than useless) under dynamic flexing as in natural rubber. The effects of mineral loadings and of mineral rubber are also similar to those described under natural rubber; that is, they reduce the efficacy of wax additions. With these restrictions in mind the overall picture shows increased weathering resistance over that of natural rubber.

Other Synthetics.—Buna-N (GR-A) is similar to natural rubber in its susceptibility to atmospheric ozone and in its protection by wax. Neoprene-FR is also similar to natural rubber in these respects, as might be anticipated from its polyisoprene content

Butyl rubber (GR-I) appears to be unaffected by concentrations of ozone much higher than atmospheric, a natural consequence of its low unsaturation.

Neoprene-GN (GR-M) is generally considered to be ozone-resistant, but this designation calls for qualification. Gum or high-gum-content compounds are quite resistant to fairly high concentrations of ozone; but if diluted by heavy loading or undue amounts of plasticizer or softener, they crack destructively on long exposure to the atmosphere. Large additions of dibutyl phthalate or sebacate, for example, for low temperature control should be regarded with suspicion in this connection.

The susceptibility to light-energized oxidation of these substances has not yet been evaluated.

ACCELERATED WEATHERING

Having determined the causes of weathering, we are now able to outline the requirements of an artificial weathering device to assess the possibilities of acceleration without distortion, and to diagnose the failure of existing devices properly to duplicate outdoor weathering. The device must furnish a light source, a supply of ozone, and a supply of water. It is not now believed that the kind of light source is critical; however, it is advisable to adhere as closely as possible to the range of wave lengths present in sunlight, since shorter wave lengths are totally absorbed by a much thinner layer of rubber, and so tend to restrict oxidation to a purely surface layer. The source must not permit the ambient temperature to rise above 100° F; otherwise some means of cooling must be adopted. The exposure to light should preferably be intermittent, with a dark period sufficiently long to allow wax to come to the surface, which may have been reabsorbed during the light exposure period (with ensuing rise of temperature of the exposed specimens). The specimens must be washed with water at intervals to remove the water-soluble material resulting from oxidation, otherwise the outdoor pattern of checking will not be duplicated. The atmosphere surrounding the specimens must contain an adequate and uniform concentration of ozone with, preferably, an upper limit of not more than about 20 volumes of ozone per hundred million of air. This is

important, for the relative performances of a series of compounds under test vary with the ozone concentration. The higher the ozone concentration, the poorer is the performance of the compounds of low resistance, compared with those of high resistance. That is, the compounds of lower resistance are discriminated against to an undue degree. For example, a certain compound containing 1 per cent of wax showed an increase in "time to crack" over the unwaxed compound of seventy-five times at a concentration of ozone of 10 parts per hundred million; at a concentration of 60 parts ozone, this ratio was reduced to 3 and with 100 parts of ozone, the ratio was 1. The brightness of the source must be balanced against the ozone concentration by trial to duplicate the appearance of specimens exposed out-of-doors under the weather conditions it is desired to simulate. Too bright a source forms a surface skin rapidly on those compounds not protected from light by carbon black or other filler, and either prevents "weathering cracking" or results in a different kind of cracking. A source of insufficient energy fails to aggravate the ozone cracks in the way described in the text

Unfortunately there seems to be no satisfactory quantitative measurement for the degree of weathering degradation. Tensile tests cannot discriminate between a single deep ozone crack in an otherwise undamaged specimen and an advanced state of light-energized oxidation without cracks.

There is no weathering device on the market to meet the requirements outlined. Of the two in current usage, one cannot generate ozone by reason of the screening of the arc, and all breakdown produced in this device is purely by light-activated oxidation. The same fact applies to the other accelerated weathering unit when the housing of special glass panels is used with the light source. Removal of the glass panels releases the short wave-lengths of light essential to the formation of ozone and an atmosphere of ozone in the tank results, which is very uneven in distribution, and varies in average concentration from 10 to 20 volumes of ozone per hundred million, depending on the efficiency of the exhaust system which can vary considerably with the duct design. However, as a result of uncovering the arc, temperatures rise to unreasonable heights with ambient temperatures of 130–140° F, depending on room temperature; temperatures of some specimens approach 200° F. As a consequence, in this device waxed natural rubber compounds show practically no protection from cracking. Furthermore, the light energy is too high to balance the ozone effect, and in spite of the moderately high ozone concentration, exposed specimens are predominantly light-oxidized. Temperatures can be reduced to usable levels by interposing a water curtain between the source and specimens, but this is very wasteful of water in summer and, in any event, does not affect the excessive brightness of the source.

A device incorporating the more fundamental requirements outlined has been in use in these laboratories for some time, with excellent results. Figure 25 is a schematic diagram comprising a cylindrical tank, T, of any desired size depending on the number of samples to be processed. Its inner surface is varinished or, preferably, waxed to prevent the catalytic decomposition of the the ozone which occurs at most metal surfaces. It is open at the bottom and raised from the floor by suitable legs. B_1 and B_2 are circular baffles suitably supported. They are 2 inches or so less in diameter than the inside of the tank and thus leave a space of an inch or so between the edge of the baffle and the inside of the tank. L is a loose-fitting lid with a central chimney in which is mounted a small electric fan, F. S_1 is a source of ultraviolet light which emits the frequencies necessary for the photochemical formation of ozone from the

oxygen of the atmosphere. S_2 is a source of light which emits a range of frequencies approximating those of sunlight and capable of some adjustment as to intensity. This light must not generate ozone. R depicts the samples of rubber to be tested, mounted on a cagelike structure which can be rotated about source S_2 to ensure uniformity of exposure from sample to sample. Fan F causes air to enter the appliance at the bottom; in the compartment below baffle B_1 it is irradiated by S_1, and a certain amount of ozone is formed. The concentration of ozone in the air leaving the compartment is determined by its volume, controlled by the speed of fan F, by the voltage fed to lamp S_1, and by the height of baffle B_1 above S_1. The ozonized air, whose course is shown by dotted lines, is drawn through the clearance between B_1 and the sides of the tank, streams over the samples under test hung around the walls, and departs *via* the clearance around B_2 and chimney C. The specimens are thus con-

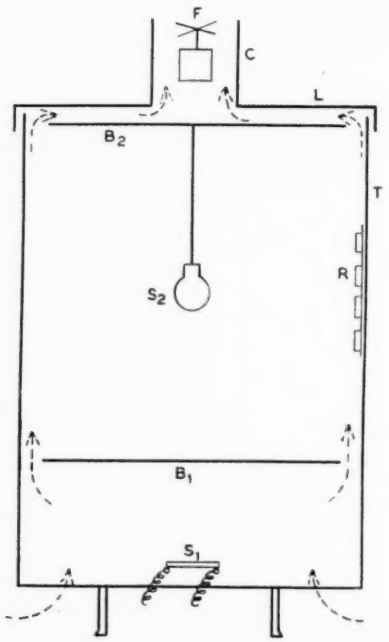


FIG. 25.—Device for Artificial Weathering of Rubber Compounds

tinually exposed to an atmosphere of ozone of the desired concentration. At the same time they are subjected to light rays from source S_2, either continuously, or if desired, intermittently by switching S_2 on and off at definite periods. When S_1 and S_2 are suitably chosen, the temperature inside the cabinet is only a few degrees above room temperature, but this can be raised to any desired degree by installing an ordinary electric light bulb or heating element in the exposure chamber. If light colored goods are to be tested, a water spray must be included to wet the samples at intervals, since light-energized oxidation is a material factor and the soluble products of oxidation must be removed if outdoor conditions are to be met. In the model currently in use, S_1, is a

Hanovia type S quartz mercury arc, S_2 is a General Electric S_4 sun lamp, the tank T is 2 feet in diameter and 3 feet high on 6-inch legs. Fan F is a 6-inch household fan. The amount of ozone generated by S_1 gradually decreases with the age of the lamp, but the output finally becomes uniform. The concentration in the exposure chamber is readily adjusted by regulating the size of the chimney orifice or the speed of the fan. In these laboratories the ozone concentration is usually maintained at 10 parts per hundred million by volume. The degree of cracking is estimated visually under a magnification of 7 to 10 times. Observation in this way is more instructive than running the test to the point of breakdown which is readily obvious to the naked eye, and makes conclusions permissible in a much shorter time

This device is not intended to furnish high acceleration of weathering but rather a moderate acceleration under uniform conditions which produce results closely analogous to those from outdoor exposure, and may be readily modified to simulate those of temperate or tropical locations. Under the conditions described, acceleration is from three to four times that of summer aging in this locality. Since, in these laboratories, interest is largely confined to the performance of compounds under low orders of stress, sheet specimens are exposed as strips stapled to a lacquered board under 10, 20, 30, and 50 per cent elongation or as loops in the manner of A.S.T.M. Test D518–44. Insulated wires are wound on mandrels of sizes calculated to produce the same range of elongation, as in the sheets. Performance is gauged by the time taken for cracks to appear in comparison with standard compounds of known weathering characteristics

Investigations are under way to determine the feasibility of evaluation by physical tests. However, it is unlikely that weatherability can be assessed in terms of a single index of merit, because of the varied usages to which rubber lends itself. Where the article is not subject to extension, susceptibility to light-energized acceleration is the important factor, and in such cases the rate of oxidation under standardized conditions of illumination and temperature, determined by a simple manometric or gravimetric test, classifies a compound in a few hours. As Figures 8 and 9 show, this does not tell the whole story, but in the case of a natural rubber compound at least the early stages of oxidation place it in one of the three groups; its subsequent behavior can be anticipated accordingly. Similar curves are being determined for the synthetics. Where the rubber in the compound is protected from light by enough carbon black or ferric oxide, exposure to an ozone-charged atmosphere alone, without illumination, is sufficient; and the compound is rated in terms of time taken to crack, compared with the reference compound, for a given concentration of ozone. There is a pitfall in this connection, however, especially in the case of GR-S compounds. In a high-quality GR-S compound such as a cable jacket, as little as 2 per cent of an effective wax will, at 25 per cent elongation and at room temperature, protect the compound for weeks from ozone of a concentration as high as 100 parts per hundred million. Discrimination between this and larger additions of wax is, therefore, not possible in such circumstances. Differences do appear at higher elongations—hence the need for observations at different degrees of stretch. Raising the temperature also shows up differences in wax concentration, and there are indications that reasonable discrimination can be made in this way. This feature is now under study.

These tests can lead to reliable conclusions as to the weatherability of a rubber compound, but experience and good judgment are still called for in making such appraisal.

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PROPERTIES OF HARD RUBBER. XIV. INFLUENCE OF SOME INGREDIENTS ON SURFACE DETERIORATION IN SUNLIGHT *

H. F. Church, L. H. N. Cooper, and H. A. Daynes

INTRODUCTION

It is known that the decrease in surface resistivity which hard rubber undergoes is due to the formation of sulfuric acid on the exterior of the dielectric, but there is little definite information in published literature as to the influence of various ingredients on the rate of formation of an acid conducting film on the surface of hard rubber when exposed to sunlight. Apart from the tests of Hartshorn, who found a loaded material, *i.e.*, hard rubber containing mineral or foreign ingredients other than rubber and sulfur, to be much superior to an unloaded one, statements as to the prevention of deterioration by loading are not generally supported by the results of quantitative experiments. Two of the present authors have investigated fully the behavior of an unloaded and a loaded material, and found the latter to retain its insulating properties better at 75 per cent relative humidity, but not so well at the highest humidities[1]. In this case, however, the composition of the loaded material was not known. In view of the knowledge that the decrease of surface resistivity is due to the formation of sulfuric acid, some exposure tests have been made on hard rubbers containing various ingredients which react with sulfuric acid to form insoluble sulfates.

EXPERIMENTAL

Method of test.—The methods of exposure and measurements of surface resistivity adopted in these experiments were briefly as follows. Thin strips of the material were prepared and provided with Aquadag electrodes among their longest edges. The strips were mounted in Vitaglass tubes, in which the humidity of the air was kept at 75 per cent relative humidity by the presence of moist sodium chloride, and connecting leads were brought out through wax plugs at the ends of the tube. The tubes were exposed simultaneously to daylight, with one face of each strip pointing in a common direction towards the north. The resistance was measured at intervals during the exposure, in each case after conditioning in the dark for a definite time, by the electrometer method already described[2]. The effective exposure was measured approximately by the darkening of a photographic paper, and is expressed in units defined as *standard hours* of sunlight.

First series of tests. Effect of small percentages of inorganic ingredients.—A blank mixing of rubber 68 and sulfur 32 was made, and other samples were prepared by the addition of small percentages of various acid-neutralizing ingredients, as shown in Table 1. The quantities are given as percentages,

* Reprinted from the *Journal of Rubber Research* (The Research Association of British Rubber Manufacturers), Vol. 14, No. 10, pages 155–159, October 1945.

TABLE 1

Sample		Added ingredient	Percentage	Vulcanization, (hrs. at 153° C)
H3	1	Nil	0	5½
	2	Litharge	1	4
	3	Litharge	1	7½
	4	Barium carbonate	0.5	5½
	5	Barium carbonate	2	5½
	6	Calcium carbonate	1	5½

calculated on the total rubber and sulfur. Vulcanization was carried out in a platen press for 5½ hours at 153° C, after 1 hour temperature rise at a uniform rate from 100° C, except in the case of the litharge-accelerated compound, for which a shorter period of 4 hours was used as well as a longer one of 7½ hours.

The results are shown in Table 2. It has been explained in previous reports that the initial value of the resistivity is largely determined by the conduction through the body of the material, so that it is referred to in the table as "apparent surface resistivity". It may also be recalled that there is an initial period of about 5 standard hours during which there is no appreciable fall in resistivity.

TABLE 2

Sample		Initial apparent surface resistivity at 75 per cent relative humidity $\times 10^{18}$ (ohms)	Period in standard hours to reach surface resistivity (ohms) at 75 per cent relative humidity					
			10^{18}	10^{16}	10^{14}	10^{12}	10^{10}	10^{8}
H3	1	2.4	5.0	7.5	10.0	14.7	22	36
	2	3.5	5.5	8.8	12.7	18.3	26	40
	3	5.3	5.5	8.5	11.4	15.7	22.5	36
	4	8.0	5.8	8.0	10.8	16.1	23.8	36
	5	2.5	5.0	7.3	10.0	14.7	20.5	33.5
	6	8.0	5.5	7.5	10.0	14.0	21.5	34.3

It will be seen that there is no great improvement resulting from the incorporation of any of the ingredients. The deterioration appears to be slightly slower with Samples 2, 3, and 4, the effect being greatest with 2, *i.e.*, 1 per cent litharge, and vulcanization for 4 hours, but there appears to be no indication of any general and substantial improvement from the incorporation of small percentages of ingredients of the class examined.

Second series of tests. Effect of higher percentages of inorganic ingredients.— A second series of samples was prepared by adding 20 per cent of various ingredients calculated on the total rubber and sulfur which were in the ratio 65/35. The samples were wrapped in tin foil and vulcanized in the autoclave at 153° C for 6 hours, except the sample containing litharge, which was vulcanized for only 4¼ hours. In case the addition of such a large percentage of filler should affect the course of the deterioration other than by interaction with the acid, for example, by interfering with the penetration of light or modifying the electrical conduction conditions over a slightly acidulated surface, an inert filler, barium sulfate, was included in the series. The details of the samples are shown in Table 3

TABLE 3

Sample		Added ingredient	Vulcanization (hrs. at 153° C)
H6	1	Nil	6
	2	Barium carbonate	6
	3	Barium sulfate (pptd.)	6
	4	Calcium carbonate (whiting)	6
H7	2	Litharge	4¼

The results of the exposure tests are shown in Table 4.

TABLE 4

Sample		Initial apparent surface resistivity $\times 10^{17}$ (ohms)	Period in standard hours to reach a surface resistivity (ohms) at 75 per cent relative humidity				
			10^{16}	10^{14}	10^{12}	10^{10}	10^{8}
H6	1	1.0	7.0	11.0	18.7	35	58
	3	1.0	7.0	10.6	14.8	20	32
	3	0.7	5.0	7.5	10.7	14.4	21.5
	4	0.7	5.2	9.0	14.0	22.0	62.5
H7	2	1.0	8.0	14.0	19.3	25.2	50

It is to be noted that in this second series of tests the initial resistivity was considerably lower than in the first series. This cannot be attributed to the high percentage of fillers, for the blank mixing also showed the low value. Moreover, the blank mixing deteriorated less rapidly than in the first series, especially during the later stages. These differences may, perhaps, be due to the use of crepe instead of smoked sheet in the second series of samples. The slower deterioration might be due also to variations in the arbitrary method of measuring the effective exposure, although the difference in rate of deterioration is larger than is usually observed between successive exposure curves for one material. These differences call for further investigation.

So far as the effect of the added ingredients is concerned there was practically no improvement, but rather the reverse. At one stage the litharge sample H7 2 was better than the blank, but this advantage was not maintained. The whiting-compounded sample H6 4, also, after it had reached about 10^9 ohms deteriorated much less rapidly than the blank. On the whole, however, more was lost than gained by using these ingredients, although it is probable that some useful reaction takes place between the basic ingredients (barium and calcium carbonates and litharge) and the sulfuric acid, since the barium sulfate sample was definitely the worst, but the neutralizing effect, if any, was insufficient to bring the performance of the loaded material up to that of the unloaded blank.

There is one aspect of the question which calls for further experiments, and which was pointed out in an earlier report[1], *viz.*, that in loaded materials partial recovery may take place after removal from light, apparently due to a slow reaction between the basic ingredients and the acid formed. Whereas in bright sunlight the acid may be formed too rapidly to be neutralized, there is a possibility that, when deterioration is less rapid, the formation of acid may be prevented from affecting the surface resistivity seriously for a long time. With this possibility in view, the samples, after reaching a low resistivity of about 10^8 ohms, were allowed to rest in the dark for 26 days, and further measurements were made at intervals. The results are shown in the following table.

TABLE 5

Sample		Surface resistivity in ohms $\times 10^6$ after recovery			
		Overnight	8 days	14 days	26 days
H6	1	48	265	96	60
	2	15.7	24.7	29	35
	3	6.0	7.2	8.4	9.6
	4	194	543	1260	1920
H7	2	20.6	26.5	32.5	36

These results are in some respects difficult to interpret. The blank mixing showed a sharp recovery in the first 8 days, but returned slowly almost to its original deteriorated condition. The barium sulfate sample H6 3, contrary to expectation, showed appreciable recovery. All the samples except the blank showed a steady recovery which did not appear to approach finality even after 26 days. The calcium carbonate sample H6 4, however, was outstanding in that the increase of resistivity was much greater, namely in a ratio of about 1 to 10, compared with 1 to 1.6–2.2 for the other samples. It is concluded that, while none of these ingredients was capable of checking the rapid formation of acid or neutralizing its effects sufficiently rapidly in bright daylight, some of them might be effective in maintaining the insulating properties of the material when exposed to less intense light, or when short periods of bright light alternate with comparatively long periods of darkness or light of low actinic intensity.

Third series of tests. Surface treatment with benzidine, and incorporation of benzidine and its derivatives.—Some tests were made with benzidine, which is known to form a water-insoluble sulfate, but as its behavior during vulcanization was unknown, attempts were first made to introduce it by surface treatment with solutions.

(i) Five test strips were prepared from a high-grade unloaded commercial hard rubber, and four of them were subjected to surface treatment with solvents and solutions of benzidine; the fifth was kept untreated for comparison purposes: (1) blank, untreated; (2) benzene at 50° C for 5 hours (benzene blank); (3) saturated solution of benzidine in benzene at 50° C for 5 hours; (4) distilled water at 100° C for 7 hours (water blank); (5) saturated solution of benzidine in distilled water at 100° C for 7 hours.

Each sample was then washed with the appropriate solvent. Benzene was removed by allowing the samples to stand *in vacuo* over charcoal and paraffin wax until no further loss occurred. Water was removed by vacuum desiccation over sulfuric acid. The samples were not touched by hand and were not visibly harmed by the treatment. The results of the tests are shown in Table 6.

TABLE 6

Sample	Initial apparent surface resistivity $\times 10^{18}$ (ohms)	Period in standard hours to reach a surface resistivity (ohms), at 75 per cent relative humidity				
		10^{18}	10^{16}	10^{14}	10^{12}	10^{10}
1	200	6.0	8.3	10.4	13.5	21
2	8	8.5	11.5	13.5	18.8	26.5
3	0.00005*	—	—	—	23.0	29.5
4	0.5	—	6.2	9.7	13.0	21
5	5	10.3	10.9	11.2	15.3	27

* Low initial value remained constant for about 15 standard hours.

It will be seen that all the treatments with solvents or solutions decreased the initial resistivity, but not to a low value except in the case of Sample 3.

The material deteriorated less rapidly after the benzene treatment, but rather more rapidly after the water treatment.

The rate of deterioration after treatment with a benzidine solution was in both cases lower than that of the material either untreated or treated with the solvent alone. The effect was quite appreciable, considering that the quantity of benzidine left in the surface must have been very small. Of the two solvents, benzene was the more efficient.

(ii) To confirm these results a second, somewhat similar series of tests was made, the samples being treated as follows:

(1) Distilled water at 100° C for 1 hour
(2) Distilled water at 100° C for 7¾ hours } Water blanks
(3) Saturated solution of benzidine in water at 100° C for 1 hour
(4) Saturated solution for benzidine in water at 100° C for 7¾ hours
(5) Benzene at 40° C for ¾ hour
(6) Benzene at 40° C for 3½ hours } Benzene blanks
(7) Saturated solution of benzidine in benzene at 40° C for ¾ hour
(8) Saturated solution of benzidine in benzene at 40° C for 3½ hours

After treatment, Samples 6 and 8 had buckled badly and were very flabby, so no electrical tests were made. The benzene solutions in these cases had also become yellow, due to the extraction of soluble substances from the samples. The remaining six samples were tested, with the results shown in Table 7.

TABLE 7

Sample	Initial apparent surface resistivity $\times 10^{16}$ (ohms)	Period in standard hours to reach a surface resistivity (ohms) at 75 per cent relative humidity				
		10^{13}	10^{15}	10^{14}	10^{12}	10^{11}
1	0.0063	—	—	—	8.4	11.0
2	0.63	—	—	6.5	8.7	11.2
3	4.5	—	8.5	9.8	13.5	18
4	0.0056	—	—	—	12.5	16
5	71	—	5.4	6.6	9.5	12.5
7	160	3.6	6.6	8.3	12.5	16

The worst cases of interference with the initial surface resistivity were those treated with water or the aqueous solution, where surface marking was observed. The low initial resistivity observed in the previous series after treatment with the benzene-benzidine solution was not here confirmed, this sample being the best of the present series.

As far as rate of deterioration is concerned, there appears to be little difference between the effects of the treatments with the solvents or between the treatments with the solutions, but the samples treated with solutions were definitely better as a group than those treated with the solvent alone, thus confirming the anticipated beneficial action of the benzidine.

(iii) An attempt was next made to produce hard rubber containing 0.5 per cent benzidine added as an ingredient in the ordinary way. The benzidine was added as a 5 per cent master batch, to part of a base stock of rubber and sulfur (65/35). The remainder of the base stock was remilled to make it comparable with the benzidine-compounded stock. Both stocks were then vulcanized in a platen press for various periods at 153° C after a 1½-hour rise from 120° C. The samples were then tested for content of free sulfur; the results are shown in Table 8.

TABLE 8

Mixing	Vulcanization (hrs. at 153° C)	Free sulfur (%)
65/35	5	4.02
	6¼	3.32
	7½	3.14
65/35 with 0.5% benzidine	5	3.09
	6¼	2.88
	7½	2.72

Judging by the percentage of free sulfur, the benzidine appears to have acted as an accelerator, the free sulfur after 5 hours' vulcanization with benzidine being equal to that after about 7½–8 hours' vulcanization without it. The estimate of the equivalent vulcanization periods for the two mixings, however, is subject to some correction according to the extent to which the sulfur reacts with the benzidine and fails to appear as free sulfur in the analysis of the acetone-extractable substances.

Tests for the presence of unchanged benzidine in the vulcanizates were made (*a*) by extracting raspings of all the benzidine-compounded samples and, as a blank, the 6¼ hour rubber-sulfur material, with hot water for 7½ hours in a Soxhlet apparatus and (*b*) by extracting the 5 and 7½ hour samples with acetone for 16 hours in the Schidrowitz apparatus and then extracting the acetone extract with hot water. In no case was benzidine detected either by precipitation as sulfate or by coloration with bromine water.

(iv) It was thought possible that some less reactive derivatives of benzidine might be found which would withstand vulcanization better than benzidine itself and yet be equally effective in forming an insoluble sulfate with the acid produced on exposure of the material to light. Samples of *s*-diformylbenzidine, *s*-diacetylbenzidine and diphenylenedimethane (*s*-dicarbethoxybenzidine) were prepared and used to make the following six mixings, the stated proportions being added in each case to 100 parts of a 68/32 rubber-sulfur stock: (1) nil; (2) diformylbenzidine, 0.5; (3) diformylbenzidine, 2.0; (4) diacetylbenzidine, 2.0; (5) diphenylenedimethane, 0.5; (6) diphenylenedimethane, 1.5.

The mixings were given 1¼ hours' rise from 110° C, and vulcanized in the platen press for 1½ hours at 153° C. They were then wrapped in tinfoil and vulcanized for a further 4 hours in the steam pan at 153° C. At the time of wrapping in tinfoil Sample 2, and still more Sample 3, appeared more advanced in vulcanization than the other three samples, indicating that diformylbenzidine is a comparatively rapid accelerator. At the end of vulcanization, Sample 4 had completely disrupted in the middle, while sample 5 had developed a pronounced swelling with a porous interior. The remaining specimens remained intact, including Sample 6, which contained three times as much of the dimethane as 5. Whether these effects were due to decomposition of the benzidine derivative or to internal heating due to the rapid development of the exothermic reaction between the rubber and sulfur is uncertain.

In all cases it was possible to obtain test-pieces for light deterioration tests. The results of these are shown in Table 9.

TABLE 9

Sample	Initial apparent surface resistivity $\times 10^{18}$ (ohms)	Period in standard hours to reach a surface resistivity (ohms) at 75 per cent relative humidity				
		10^{18}	10^{16}	10^{14}	10^{12}	10^{10}
1	3.5	6.0	8.5	12.0	17.5	25
2	1.4	4.3	7.1	9.5	13.2	20
3	7.9	5.5	8.0	11.2	15.6	22.5
4	5.3	5.0	7.1	9.5	13.2	20
5	4.4	5.3	8.3	10.5	15.0	22
6	3.8	5.0	8.0	10.0	14.0	21

Although there were some slight differences between the rates of deterioration, in no case was the material containing the benzidine derivative better than the simple rubber-sulfur mixing.

It seems, therefore, that benzidine might be effective in neutralizing the acid formed by hard rubber in daylight, but that no practicable method of introducing it and retaining it in a suitable form during vulcanization can be recommended. The present simple experiments, however, are clearly not exhaustive.

SUMMARY

Experiments have been made to find to what extent ingredients capable of reacting with sulfuric acid to form insoluble sulfates can prevent the loss of insulating properties of hard rubber on exposure to daylight.

Hard rubbers containing small and large percentages of calcium and barium carbonates and litharge have been tested, along with a comparable unloaded material and one containing an inert filler, barium sulfate.

In no case was there a substantial improvement. Although the basic fillers gave better results than the inert filler, the samples containing them were inferior to the unloaded sample.

The partial recovery of insulating properties on removal from light after a low surface resistivity has been reached has been investigated. Appreciable recovery took place in all cases, but this was most marked with the sample containing calcium carbonate. It was anticipated that the basic ingredients examined would to some extent prevent the undesirable effects of acid formation in cases where the exposure to light was not continuous or so severe as bright north daylight. Further experiments on this point are recommended.

The value of benzidine as an ingredient which forms an insoluble sulfate was tested by treating the surface of hard rubber with aqueous and benzene solutions of this material. Appreciable improvement was observed in each case. Attempts to prepare vulcanizates containing benzidine or derivatives of it having the same protective effect were unsuccessful.

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PROPERTIES OF HARD RUBBER. XV. INFLUENCE OF RUBBER-SULFUR RATIO AND VULCANIZATION TIME ON THE PROPERTIES OF PURE RUBBER-SULFUR COMPOSITIONS. (1) CHEMICAL COMPOSITION, DENSITY, AND THERMAL EXPANSION *

H. F. Church and H. A. Daynes

ORIGIN AND ORGANIZATION OF THE RESEARCH

Hard rubber (ebonite, vulcanite) is one of the oldest established of the high-grade insulators and has been widely used as a typical dielectric in scientific research, as will be seen in a summary of literature on its physical properties. In many respects it approaches the ideal, but there are two outstanding weaknesses which seriously limit its field of use. One of these is the tendency for the surface to become acid, and therefore conducting, on exposure to sunlight. This has been reported by many observers, and the Research Association of British Rubber Manufacturers since its early days has made the fundamental study of this problem a prominent item in its program of research. The other weakness of hard rubber, probably a more serious one, is its tendency to soften at high atmospheric temperatures.

The present joint investigation arose out of a Conference on Insulating Materials called on the recommendation of the Radio Research Board, held on February 8, 1926, at the Department of Scientific and Industrial Research. At that date the Conference agreed that the field of research in which useful work could be done was enormous, but it was considered that ebonite and the allied rubber class of materials were the most promising for investigation. "In this class," the report of the Conference states, "an ideal material would be one which maintained high insulating and mechanical properties of good ebonite, but which: (1) had a coefficient of expansion in the neighborhood of 30×10^{-6} and did not soften or warp with temperatures up to 180° F; (2) had a greatly increased mechanical strength; (3) did not sweat or deteriorate with prolonged exposure to sunlight. A low specific gravity would also be a desirable feature."

In the discussion, the R.A.B.R.M. offered to assist in further work by making up any special samples of hard rubber required, and the British Electrical and Allied Industries Research Association (E.R.A.) offered to organize a representative supervisory committee to arrange for tests on the materials prepared.

Under this arrangement the R.A.B.R.M., in June, 1928, prepared a memorandum outlining a proposed program of research and drew attention particularly to (1) the necessity for studying simple rubber-sulfur compositions as the

* Reprinted from the *Journal of Rubber Research* (The Research Association of British Rubber Manufacturers), Vol. 14, No. 11, pages 165–172, November 1945.

first stage; (2) the advisability of studying at an early stage the influence of the method of preparation of raw rubber on the physical properties of the vulcanizate; and (3) the probability that the water-soluble components of the raw rubber would affect the electrical properties by controlling the content of absorbed moisture under given atmospheric conditions. In regard to (3), work carried out by the R.A.B.R.M. had already indicated that absorbed moisture is an important factor in determining dielectric losses in hard rubber, and it was thought that this offers a likely explanation of the changes in power factor of hard rubber after manufacture, which had been observed by D. W. Dye of the National Physical Laboratory.

Joint research was then undertaken, in which both the R.A.B.R.M. and E.R.A. contributed financially, while the London Advisory Committee for Rubber Research (Ceylon and Malaya) assisted by supplying specially prepared plantation rubbers as necessary. Since the R.A.B.R.M. had facilities both for making the special samples of hard rubber and for carrying out most of the chemical and physical tests, it was decided that the bulk of the work should be carried out in its laboratories at Croydon, only electrical tests requiring specialized apparatus or technique being carried out elsewhere; for example, at the National Physical Laboratory.

GENERAL PLAN OF THE WORK

It was clearly impossible to plan such a comprehensive research in detail, but the general lines of the work were laid down in accordance with the following guiding principles.

1. The main object of the work was to obtain data on the effects of the usual variables in manufacture and to explore the possibility of improving hard rubber in certain respects as indicated by the Radio Research Board. It was decided that fundametal researches into the nature of the reaction between rubber and sulfur and of the physical structure of the vulcanizate, although they might lead to a solution on unexpected lines, should be provided for in other ways, and should not retard the following of a program laid down on broad lines by the supervisory committees.

2. It was anticipated that hard rubber might not be improved in the required directions without the addition of materials other than rubber and sulfur. On the other hand, the influence of additional ingredients could not be effectively studied without a preliminary investigation of the simple rubber-sulfur compositions, which would always form the dispersion medium for these added materials. Moreover, there was reason to believe that the water-soluble components of raw rubber, which vary with the method of preparation, would have an important influence on the electrical properties of the vulcanizate, not only initially, but also to a variable extent according to humidity conditions.

3. Since it was important that the results of tests should be comparable at all stages of the work, testing methods for all the properties in question had to be decided upon before the commencement of the main program of work. In some cases, new methods had to be developed. Also, to ensure uniformity of raw materials, sufficient stocks of raw rubber and sulfur for all the work on unloaded hard rubbers had to be set aside after each had been thoroughly mixed.

4. There is already a considerable literature on the properties of hard rubber in relation to composition and degree of vulcanization, but in most cases only one or two properties had been studied in each material. In the

present work the intention was to find whether various desirable properties could be combined in a single material and to what extent the production of a material for a particular purpose was a matter of compromise involving the sacrifice of otherwise desirable features. Owing to the variety of compositions tested and methods used in previously published work, it was impracticable to reach safe conclusions on this point without further experimental work. One feature of the program, therefore, was that each material would be submitted to a variety of both mechanical and electrical tests, including plastic flow and surface deterioration in which improvement was particularly desirable. In order that these tests should be carried out on identical material, it was decided that the samples should be prepared simultaneously in sheets of one thickness, all the methods of test being selected so that test-pieces could be cut therefrom instead of being moulded in various shapes and thicknesses. Moreover, in order that the sheets should be uniform throughout their thickness, the thickness was to be selected (according to the results of preliminary tests with thermocouples in the material) to ensure the absence of appreciable internal heating resulting from the exothermic reaction between rubber and sulfur during vulcanization.

In accordance with the above considerations the following general plan was adopted.

Literature.—Preparation of comprehensive summary of published literature on mechanical, electrical, and other physical properties.

Experimental

I. Variation of unloaded rubber-sulfur compositions.
   (*a*) Rubber-sulfur ratio and degree of vulcanization.
   (*b*) Temperature of vulcanization.
   (*c*) Method of vulcanization.
II. Variation of raw rubber.
III. Addition of other ingredients.

The summary of literature has already been completed. The experimental work of Part I (*a*) is described in the present report.

A list of properties on which information was desirable and from which selection could be made was prepared as follows: (*a*) (i) Total sulfur and (ii) free sulfur; (*b*) plastic yield; (*c*) brittleness; (*d*) density and coefficient of expansion; (*e*) cross-breaking strength; (*f*) water absorption at equilibrium; (*g*) electric strength; (*h*) (i) permittivity and (ii) power factor; (*j*) (i) volume resistivity and (ii) surface resistivity; (*k*) chemical action on brass and copper; (*l*) tensile strength; (*m*) scleroscope resilience; (*n*) influence of the following factors on properties (*a*) to (*m*) above: (i) temperature (*e.g.*, 10, 30, 50, 80° C); (ii) aging due to continued heating in air at 65° C and 80° C (tested cold); (iii) exposure to light; (iv) exposure to humid atmosphere; (v) immersion in oils, acids, alkalies, and selected solutions (*e.g.*, brine).

EXPERIMENTAL. I(*a*) VARIATION OF UNLOADED RUBBER–SULFUR COMPOSITIONS

A. Preparation of sheets.

(*a*) Materials

(i) Rubber

The rubber was part of a large consignment of washed smoked sheet, as used for all R.A.B.R.M. laboratory work. Except where otherwise stated, this

rubber, averaged in the following way, was used; 180 pounds of sheets was taken, and each sheet was divided into three parts and used to make three average batches A, B, and C of 60 pounds each. B and C were stored in the dark for later investigations, and batch A was treated thus: (1) It was divided into 10 equal parts of 6 pounds, each part being partially milled and sheeted out; (2) each milled 6-pound sheet was divided into 10 equal parts and used to make 10 average batches of 6 pounds each; and (3) each of the final 6-pound batches was well milled and stored in the dark.

(ii) Sulfur

Flowers of sulfur of one grade and delivery were averaged in the following way: 90 pounds of sulfur was divided into three lots of 30 pounds each. Each lot was divided into three equal parts and, by selecting one-third at a time from each lot, three average batches A, B, and C of 30 pounds each were formed. B and C were stored in the dark in covered bins for later investigations. The average lot A, after thorough stirring, was treated thus: (1) It was divided into three equal portions of 10 pounds each; (2) each 10 pound portion was subdivided into three equal parts and used to make three average portions of 10 pounds each and (3) the three final 10-pound portions were well stirred and stored in a closed bin.

The following analyses were made on the averaged sulfur:

Acidity.—10 grams of sulfur was moistened with alcohol, 100 cc. of water added, and the mixture titrated with 0.1 *N* caustic soda. Blank tests were made with alcohol and water only. The mean of two determinations expressed as H_2SO_4, was 0.037 per cent by weight.

Ash.—Samples weighing about 4 grams were incinerated in a crucible over a bunsen flame. The mean of two determinations was 0.005 per cent by weight.

Water content.—The loss in weight of 1.7-gram samples on storing over concentrated sulfuric acid to constant weight (96 hours) was measured. The mean of two determinations was 0.05 per cent by weight.

(*b*) Method of mixing stock

All rubber-sulfur stocks were subjected to similar milling on a small experimental mill at even speeds. They were then sheeted out to approximately the right thickness for moulding and allowed to rest for at least 24 hours before vulcanizing.

(*c*) Composition of stocks

It was decided originally to adopt three rubber-sulfur ratios, namely 65/35, 68/32 and 72/28, the mixings being called A, B, and C, respectively. At a later stage, when aging tests were to be carried out, it was found possible, in view of the results of tests already obtained on A, B, and C, to reduce the number of mixings to two, namely 65/35 and 70/30, called K and L, respectively. The stocks for these two mixings were made by remilling the residues of stocks A, B, and C, sulfur being added as necessary. As the stocks had been stored for a considerable time, it is possible that the vulcanizates are not strictly comparable with those of A, B, and C, the sheets being $\frac{3}{8}$ inch thick, instead of the usual $\frac{3}{16}$ inch. As averaged rubber could not be spared, the stocks were made up from an unaveraged portion of the same washed smoked sheet. These stocks were called P, Q, and R. The details of all the stocks referred to in the report are shown in Table 1.

TABLE 1

COMPOSITION OF STOCKS

Rubber-sulfur ratio	Stock for program I(*a*)		
	Tests on initial properties	Aging tests	Electric strength tests
65/35	A	K	P
68/32	B	—	Q
70/30	—	L	—
72/28	C	—	R

(*d*) Vulcanization

The vulcanizing temperature was 155° C in all cases. The samples were given a preliminary moulding in a daylight press in steel moulds 10 inches square internally and $\frac{7}{32}$ inch thick, the faces of the rubber sheet being in contact with aluminum foil. This moulding lasted for 50 minutes (except with P, Q, and R, which had 60 minutes) after a uniform temperature rise of one hour from 100° C to 155° C. During moulding the samples were changed in position and rotated in the press at intervals to eliminate variation due to differences in platen temperature.

After this moulding, the rubber still being in a soft condition, the samples were transferred to moulds $\frac{3}{16}$ inch thick to allow for shrinkage and stacked in an autoclave press and vulcanization completed at the same temperature after the same rise as before. In the case of sample Q, the 10 hours' vulcanization was carried out in two stages, thus involving an extra rise. The effect of the rise was estimated to be equivalent to 13 minutes at vulcanization temperature.

The total vulcanization periods at 155° C for all the stocks concerned were as follows:—

A, B, and C.....3, $3\frac{3}{4}$, 5, 7, and $10\frac{1}{2}$ hours.
K and L.....3, 5, and $10\frac{1}{2}$ hours.
Q.....$2\frac{2}{3}$, $4\frac{2}{3}$, and 10 hours.
P and R.....$4\frac{2}{3}$ hours.

Within each of these three groups of materials, sheets having the same vulcanization period were vulcanized in the press together, so that comparison between them would not be invalidated by any error in control of vulcanizing temperature. The autoclave was chosen for the final vulcanization owing to the danger of nonuniformity in the daylight press.

(*e*) Preparation of test-pieces.

Test-pieces were cut with a circular saw and finished in a shaping machine cutting in a longitudinal direction except for the dumb-bell tensile test-pieces which were finished with a fine file and sandpaper. Moulded faces were retained except for electrical test-pieces, which had to be sandpapered or machined to less than $\frac{3}{16}$ inch thick.

B. Methods of testing and results

Introduction

The methods adopted will be described, in each case a brief outline of the method and a statement of the essential working conditions being given.

In the case of each property the principal conclusions will be stated and, where possible, compared with those of other observers. The general discussion as to the relative merits of the different mixings and vulcanization times, taking into account the whole of the properties investigated and considering

the compatibility or otherwise of various properties, will form a later section of the report. The results suggest a number of questions of considerable theoretical interest. These cannot be fully discussed, but their importance will be briefly indicated as they arise so that they may be followed up by further experimental work.

In comparing with the results of other observers, only those results are admitted as truly comparable which are explicitly stated to be made from rubber and sulfur only. For example, samples stated to be "best hard rubber" are treated as of uncertain composition, and materials consisting of rubber, sulfur, and accelerator are likewise excluded, since the influence of accelerators falls in a later section of the work. References will be given to the original papers of other observers, but their principal results will be found in the summary of literature prepared in connection with this research.

1. Chemical Composition

(*a*) Methods of Test

(i) Acetone Extract

About 1 gram of each sample was finely rasped and extracted with acetone in a Schidrowitz extractor substantially as described in British Standard Specification, No. 234–1931, except that the extraction was continued to 16½ hours. The results are shown in Table 2.

TABLE 2

CHEMICAL ANALYSIS

Mixing and nominal rubber-sulfur ratio	Vulcanization, (hours at 155° C)	Total sulfur (%)	Acetone extract (%)	Free sulfur (%)	Combined sulfur (%)	Vulcanization coefficient
A 65/35	3	35.5	7.81	6.49	28.8	45.4
	3¾	—	6.03	4.90	30.4	47.8
	5	(Mean 35.25)	4.99	3.82	31.4	49.5
	7	—	4.83	3.70	31.6	49.7
	10½	35.0	4.94	3.79	31.5	49.5
B 68/32	3	32.4	5.91	4.57	27.8	42.0
	3¾	—	4.12	2.68	29.7	44.9
	5	(Mean 32.4)	3.26	1.57	30.8	46.7
	7	—	2.87	1.57	30.8	46.5
	10½	32.3	2.85	1.56	30.8	46.5
C 72/28	3	28.4	4.09	2.51	25.8	36.8
	3¾	—	2.62	1.14	27.2	38.7
	5	(Mean 28.3)	2.07	0.55	27.8	39.6
	7	—	2.01	0.35	28.0	40.0
	10½	28.2	1.89	0.27	28.0	40.1

(ii) Free Sulfur

Uncombined sulfur extractable by acetone was determined in the dried extract described above by the method described in B.S.S. 234–1931 (oxidation with fuming nitric acid and potassium perchlorate). The results are shown in Table 2.

(iii) Total Sulfur

The total sulfur in the hard rubber was controlled in mixing, but as a check on this process a chemical determination was made on certain samples by the Carius method as described in B.S.S. 234–1931. The results are shown in Table 2.

(iv) Combined Sulfur

The percentage of rubber-combined sulfur was not determined directly, but calculated by difference between the percentage of free sulfur and the mean percentage of total sulfur for the mixing as determined in (iii).

(v) Vulcanization Coefficient

The vulcanization coefficient was not determined directly by estimations of hydrocarbon and rubber-combined sulfur, but was calculated in the form

$$\frac{\text{per cent combined sulfur} \times 100}{100 - \text{per cent combined sulfur} - \text{per cent acetone extract}}$$

(*b*) Discussion of Results

The chemical analyses were made mainly to obtain an indication of the degree of vulcanization so that materials of different composition might be compared at corresponding states. It was anticipated that this would be sufficiently indicated by the vulcanization coefficient. Apart from this consideration, the results of the analysis are not interesting as representing properties of direct practical importance except, perhaps, the percentage of free sulfur, which may have a bearing on questions of corrosion of adjacent materials.

In discussing the results it must be remembered that the vulcanization coefficient (v.c.) was determined indirectly, so that it is only an approximation subject to certain errors which will be mentioned below.

Vulcanization coefficient and percentage of free sulfur are plotted against vulcanization period in Figures 1 and 2, the curves for the three mixings being distinguished by their letters A, B, and C.

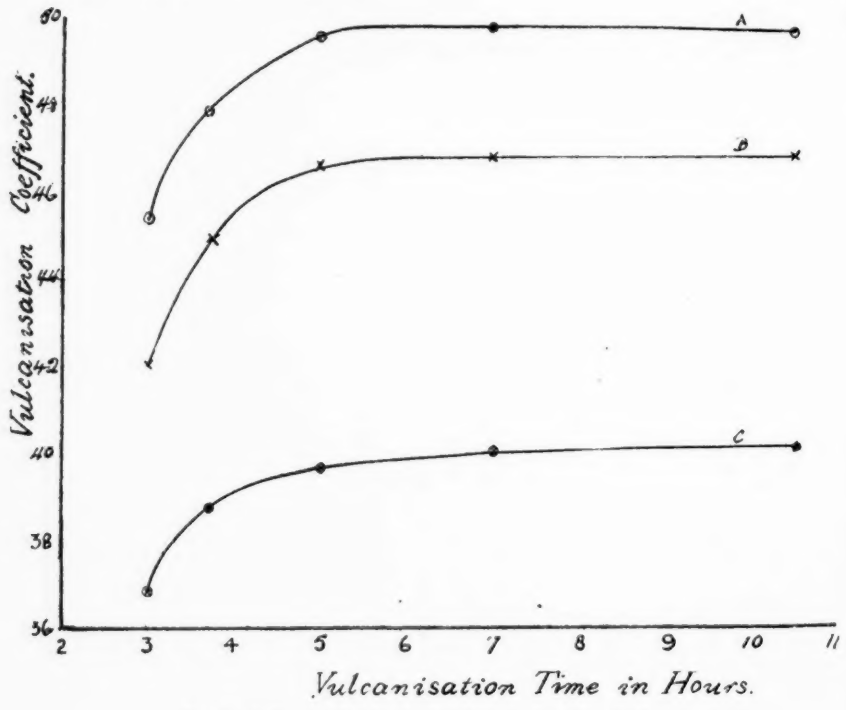

FIG. 1.—Influence of vulcanization time on the vulcanization coefficient of materials A, B, and C.

Influence of Vulcanization Period.—It is seen from Table 2 and the graphs that the uncombined sulfur decreases with increasing vulcanization period and approaches a limit which depends on the rubber-sulfur ratio. The vulcanization coefficient, which depends directly on the determination of free sulfur, shows an increase of the same type.

In the two mixings, A and B, where there is more than sufficient sulfur to form the compound $(C_5H_8S)_n$ the free sulfur, and vulcanization coefficient remain substantially constant from 5 to 10½ hours, whereas in mixing C, which is deficient in sulfur, combination continues, the free sulfur tending to approach zero.

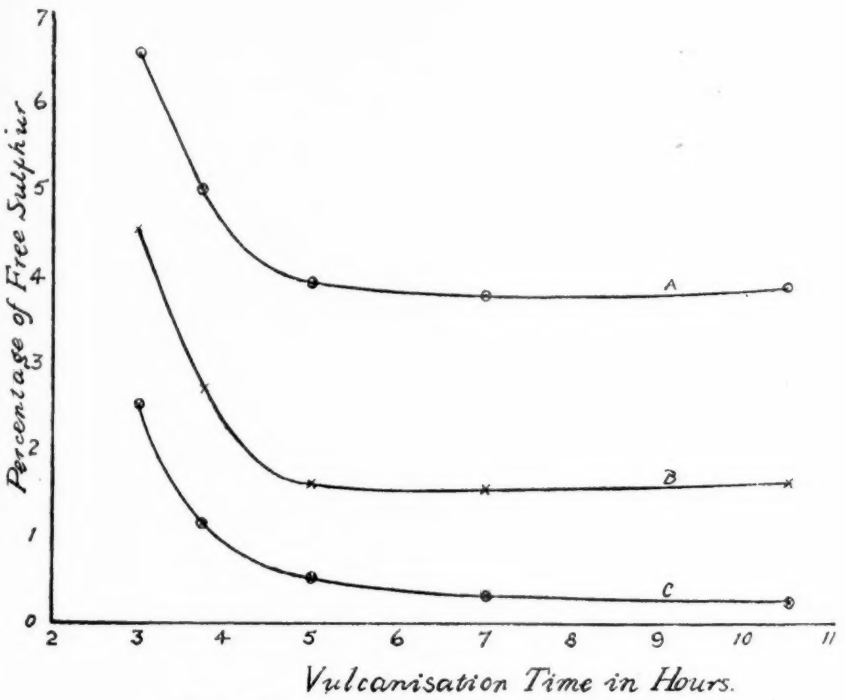

FIG. 2.—Influence of vulcanization time on the free sulfur of materials A, B, and C.

Influence of Rubber-Sulfur Ratio.—The limiting vulcanization coefficient depends on the rubber-sulfur ratio being higher the greater the percentage of sulfur. In mixing A it is greater than the theoretical value for the compound $(C_5H_8S)_n$. This is in accordance with the observations of a number of other investigators[1], the excess being attributable to (1) the formation of substitution products with loss of hydrogen sulfide, and (2) the formation of insoluble sulfur compounds of nonhydrocarbon components of the rubber.

The limiting free sulfur is higher for A than for B, as might be expected, but the difference is less than if the two mixings had the same limiting vulcanization coefficient. The fact that sulfur combination continues beyond 5 hours in mixing C, but not in A and B, has been noted above.

Criterion of Degree of Vulcanization.—It is clear that the vulcanization

coefficient, as determined here, cannot be used as a means of defining degree of vulcanization in comparing different mixings. For example, the limiting vulcanization coefficient for B corresponds to a comparatively undervulcanized condition in A, although there is excess sulfur present in both cases. It may be more useful to adopt as a criterion the degree of approach of the vulcanization coefficient (or free sulfur) to its final or limiting value, although this involves difficulties where sulfur is deficient, as in C. Reference may be made to Figure 3, in which (limiting v.c.—actual v.c.) is plotted against vulcaniza-

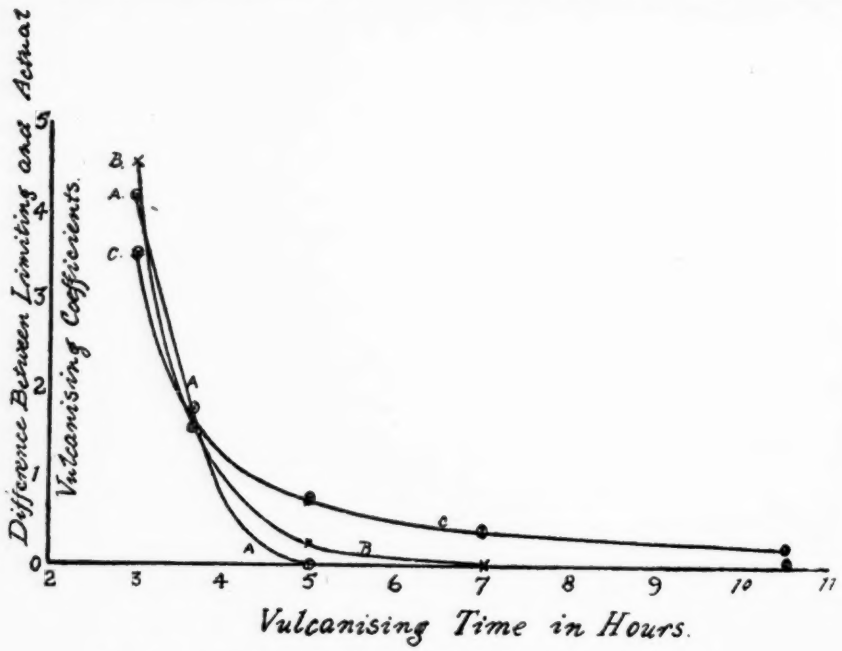

FIG. 3.—Variation, with vulcanization time, of the difference between the limiting and actual vulcanization coefficients of materials A, B, and C.

tion time. Judged by this criterion, A and B reach equivalent degrees of vulcanization in equal times, but the curve for C is of different form, crossing those for A and B and showing a slower approach to the limit. It appears that a distinction must be made between low-sulfur and high-sulfur materials in this respect and the question will be considered again in connection with plastic flow, which appears to be the most definite physical indication of degree of vulcanization.

2. Density

(*a*) Method of Test

Density was determined by weighing a specimen approximately 37 × 19 × 5 mm. in air and in water at 15° C. The results are given in Table 3.

(*b*) Results

(*c*) Discussion of Results

Influence of Vulcanization Time.—The density of each mixing increases with increasing vulcanization time, but the change after 5 hours is slight. The large contraction on vulcanization is well known and has to be allowed for in

TABLE 3

DENSITY AT 15° C

Mixing and nominal rubber-sulfur ratio	Vulcanization (hours at 155° C)	Density at 15° C (g. per cc.)
A 65/35	3	1.195
	3¾	1.198
	5	1.199
	7	1.200
	10½	1.201
B 68/32	3	1.172
	3¾	1.174
	5	1.176
	7	1.177
	10½	1.177
C 72/28	3	1.142
	3¾	1.145
	5	1.147
	7	1.147
	10½	1.148

manufacturing processes but most of the contraction has occurred before the stage considered in this report. The slight increase in density after sulfur combination has practically ceased is in accordance with observations by McPherson[2].

Influence of Rubber-Sulfur Ratio.—The density for a given vulcanization period increases with the percentage of total sulfur as might be expected, the differences being large compared with those between samples of the same mixing vulcanized for different times. This variation of density with rubber-sulfur ratio is in accordance with the results of Bunschoten[3], Kimura and Namikawa[4] and McPherson[2].

Other Conclusions.—The absolute values of density of the fully vulcanized hard rubbers (*i.e.*, those vulcanized till sulfur combination ceases) agree for all practical purposes (<1 per cent) with those of Kimura and Namikawa[4], McPherson[2], and Bunschoten[3] and Glancy, Wright, and Oon[5] for unloaded, unaccelerated materials.

Hard rubber is a complex mixture of rubber hydrocarbon-sulfur compound, free sulfur, and nonhydrocarbon components of the rubber. It would be of theoretical interest to determine accurately how the density of the hydrocarbon-sulfur compound depends on vulcanization coefficient, but sufficient data are not available. The effect of the nonhydrocarbon components is uncertain, as also is the state of the free sulfur. However, as the same rubber was used for all samples, the density of the rubber (including nonhydrocarbon components) and combined sulfur has been calculated on the assumption that the uncombined sulfur is of density 1.9 g. per cu. cm. and forms a simple mixture with it (McPherson has given reasons for believing that the free sulfur behaves in hard rubber as one of the lighter allotropic modifications). This density, when plotted against percentage of combined sulfur calculated on the residue after deduction of free sulfur, gives a smooth, almost linear relation, in good agreement with the corresponding results of McPherson.

The test for density was included partly as a check against the occurrence of microporosity in vulcanization. In view of the regularity of the results and the agreement with those of other observers, there appears to be no reason to suspect any serious fault of that kind.

3. Coefficient of Thermal Expansion

(*a*) Method of Test

The determination of linear coefficient of expansion (which is the coefficient of practical interest) is complicated by effects of warping and shrinkage in such directions as to relieve strains set up during moulding. Consequently, it was thought advisable to determine, by a dilatometer method, the coefficient of the true reversible volume expansion which, in the case of an isotropic material, is three times the linear coefficient. In view of the thorough investigations of McPherson[2] and Kimura and Namikawa[4], it was decided to make tests only in one sample (5 hours) of each mixing. The following is a brief outline of the method.

About 100 cc. of the material was immersed in water in a specially constructed glass vessel with a graduated tube, the rest of the vessel being entirely filled with boiled-out distilled water. The vessel itself and its contents were varied in temperature and the movements of the meniscus in the graduated tube noted. The effect of the expansion of the vessel was eliminated by a similar series of observations with the vessel entirely filled with water, the calculation of the expansion of the hard rubber then depending on a knowledge of the expansion coefficient of water. The method was satisfactorily checked by measuring in the apparatus the expansion of mercury which was already known.

The mean coefficient of expansion, γ, between temperatures θ_1 and θ_2 in terms of volume at 20° C is defined as the quantity $(V_2 - V_1/V_{20}(\theta_2 - \theta_1)$, where V_1 and V_2 are the volumes of the solid at temperatures θ_1 and θ_2, respectively. The results are shown in Table 4, the range of temperature being 20°–55° C.

(*b*) Results

TABLE 4

CUBICAL COEFFICIENT OF THERMAL EXPANSION, 20°–55° C

Mixing and nominal rubber-sulfur ratio	Vulcanization (hours at 155° C)	Coefficient of expansion $\times 10^{-6}$/1° C
A, 65/35	5	198 ± 2
B, 68/32	5	197 ± 1
C, 72/28	5	214 ± 2

(*c*) Discussion of Results

Influence of Rubber-Sulfur Ratio.—The low-sulfur (72/28) mixing has a distinctly higher coefficient than either of the other two, which resemble one another closely. This is in accordance with the observations of McPherson, whose values for the range 15°–40° C fell from 240 to 200 $\times 10^{-6}$/1° C on increasing combined sulfur from 24 to 32 per cent. For comparison it may be pointed out that the combined sulfur percentage (calculated on the residue after deduction of free sulfur to be comparable with McPherson's results) varied in the present mixings from 26.5 to 32.7 per cent.

Since only three samples were tested in this work, it is worth recalling that both McPherson[2], and Kimura and Namikawa[4] found the coefficient of expansion to be about two or three times as great with low percentages of combined sulfur, the change with sulfur content from high to low coefficient being abrupt. At ordinary temperatures the change occurred with lower values of combined sulfur than those in question here. Kimura and Namikawa found, however, that for each percentage of combined sulfur there was a change from low to

high coefficient when a certain temperture was reached, this temperature, increasing with increasing combined sulfur and being closely related to the plastic yield temperature. It should be realized, therefore, that undervulcanized hard rubber would have a much larger coefficient if used at a sufficiently high temperature, but that it would then be in a softer condition.

The absolute values for the coefficient of expansion given by Kimura and Namikawa[4] differ somewhat from those of McPherson[2] and the R.A.B.R.M. The formers' results indicate that the coefficient increases considerably with temperature rise, being about the same at 60° C, as found by McPherson and R.A.B.R.M. at 15°–40° C and 20°–55° C, respectively, but only about three-quarters of this value at 20° C. Mayer's value[6] for 64/34 material is about 5 per cent lower than the present figures for A and B, but applies to a lower temperature range 0°–18° C. An increase of coefficient with temperature is indicated.

SUMMARY

The properties of hard rubber made from rubber and sulfur, and particularly with the effects of varying the rubber-sulfur ratio and vulcanization period were studied.

Since this work is only the first stage in a much larger program of research, precautions were taken to ensure uniformity of material and comparability of results throughout; these precautions are described. The general plan of the whole program is outlined.

Materials having rubber-sulfur ratios 65/35 to 72/28 and vulcanization periods 3 to 10½ hours were prepared by vulcanization in a press at 155° C. These were tested for the following properties by methods which are described: Combination of sulfur, density, coefficient of thermal expansion, tensile and cross-breaking properties, impact strength (notched and unnotched) and permanent deformation on impact, plastic yield and yield temperature, permittviity and power factor at 1,000 kc. per sec. at room and higher temperatures, electric strength, volume and surface resistivity, changes of surface on exposure to light, absorption of organic liquids at 34° C and of water at room temperature, deterioration in air at 70° C.

The relative importance of the various properties is discussed. The effects of variation of rubber-sulfur ratio and vulcanization time on the properties of hard rubber are summarized, and an attempt is made to select the most suitable material for general purposes. In most respects it is advantageous to adopt the higher percentage (35) of sulfur and vulcanize until combination of sulfur has practically ceased (about 5 hours at 155° C) but no longer. All the best properties, however, cannot be combined in a single material, and some sacrifices in plastic yield temperature and the like have to be made if the highest impact strength is to be obtained, and *vice versa*. It appears that most requirements would be met by a selection of two mixings having high and low percentage of total sulfur, both being vulcanized to nearly constant free sulfur.

Correlations between certain properties are discussed as follows: Tensile and cross-breaking strength; impact strength and other mechanical properties; electric strength and loss factor; aging in sunlight and in air at high temperatures.

The bearing of these results on the specification of high-grade hard rubber is discussed, and the introduction of plastic yield and impact tests is advocated.

A number of recommendations as to further work are made both in completion of the present work and as a fundamental basis for future developments.

ORIGIN AND ORGANIZATION OF THE RESEARCH

It is clear that no single material is suitable for all insulation purposes. Each material has its points of strength or weakness, and the designer of apparatus has to select for each component the particular substance which can be economically produced in the required form, and which has the required good properties.

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EFFECT OF MOISTURE ON GR-S
RATE OF CURE AND PHYSICAL PROPERTIES *

IAN C. RUSH

CANADIAN SYNTHETIC RUBBER LIMITED, SARNIA, ONTARIO, CANADA

Moisture has been discussed as a factor which may give rise to variable rates of cure of GR-S. This moisture may be present in GR-S itself or in the compounding ingredients used. Accordingly, a program was initiated in the spring of 1944 to establish the influence of moisture, not only on the rate of cure of GR-S, but also on its physical properties. Since that time two papers have been published on this subject by other investigators[1]. The results reported here verify some of the conclusions drawn by these investigators but seem to be at variance with others.

In this study various proportions of water were added in the following ways: by premixing with carbon black, by adding directly on the mill rolls at the completion of normal milling, and by soaking GR-S crumb in water. Curing curves were obtained for each batch, and were used to evaluate the rate of cure. To eliminate day-to-day variations in physical properties due to error in testing methods, three batches of different moisture contents were mixed and tested on the same day. This same group was then remixed and tested on successive days until at least three batches had been tested for each moisture content and each method of addition. The averages of the individual results (stress-strain data and percentage moisture retained) on batches to which the same percentage of water was added, were then considered free from day-to-day variations.

MIXING, CURING, TESTING

All batches in any one series were mixed from the same sample of raw polymer. It should be noted here that the polymer used for different series was not the same. Before use the various samples were checked periodically for moisture content and were not used until they had reached equilibrium values of less than 0.1 per cent (here considered 0 per cent moisture). The chemical analyses of these samples are shown in Table I. To ensure uniformity, suffi-

TABLE I

CHEMICAL ANALYSIS OF SAMPLES (IN PER CENT)

	Method of Moisture Addition		
	To carbon black	On mill rolls	Polymer soaked in water
Ethanol-toluene-azeotrope extract	6.85	6.95	7.36
Free fatty acid	5.10	4.83	5.00
Free soap	0.29	0.06	0.12
Total ash	1.26	0.89	0.87
NaCl	0.85	0.75	0.65

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 38, No. 1, pages 58–61, January 1946.

cient compounding ingredients for all batches in this work were set aside. They were then desiccated as required for 24 hours before use.

One operator carried out all mixing and curing operations. Mixing was done on a 10 × 20 inch mill (gear ratio, 1 to 1.4). The official recipe of the War Production Board was used: GR-S, 100 parts; carbon, 50; BRT No. 7, 5; zinc oxide, 5; sulfur, 2; and mercaptobenzothiazole, 1.5.

In the first series moisture was added to predried carbon black immediately before mixing, and was dispersed as thoroughly as possible by hand. When wet polymer was used, the weight of GR-S per batch was varied so that exactly 100 parts of dry polymer were used. Milling times were held constant at the time specified in the official Rubber Reserve Company's procedure for testing GR-S. The additional time required to add the water directly to the mill rolls at the completion of normal mixing was roughly proportional to the amount of water added. This additional milling time probably had little effect on modulus, since the batches were first removed from the mill for weighing and thus cooled. Further, additional milling at that stage would tend to lower and not raise the modulus and would not, therefore, show up an increase in rate of cure. Curing was at 292° F.

In the first series where the moisture was added to the carbon black, the moisture retained was taken as the difference between the actual batch weight and an assumed normal dry batch weight. This assumed weight was based on some forty dry batches for which the maximum variation in weight was less than 0.08 per cent. In the second series the moisture retained was determined by weighing the mixed batches immediately before and immediately after the addition of water. In the third series the water added by soaking the GR-S crumb was determined by the standard RRC hot mill method. The water retained was then determined on an assumed normal dry batch weight as in the first series.

Stress-strain data were determined on a Scott L-6 tensile tester, which was thoroughly overhauled and cross-checked with the National Bureau of Standards machines immediately before this program started and rechecked periodically during the course of the work.

Considerable difficulty arose in this work in finding an accurate index to rate of cure. Four indices were investigated and compared: time to maximum tensile (T_{max}), time to constant modulus (M_{300} = 1000 pounds per square inch), tensile ratio (T_R), modulus ratio (M_R). Time to maximum tensile strength is inherently inaccurate because of the nature of the curve for tensile *vs.* time of cure and because of the poor reproducibility of the points of break of GR-S test strips. Time to constant modulus appears to give a good index of rate of cure if day-to-day variations in testing can be eliminated and if polymers of like gel contents are compared.

Tensile ratio[2] appears useful; it is the tensile of a marked undercure divided by the maximum tensile strength. This eliminates the first objection to "time to maximum tensile" *i.e.*, trying to pick the point at which the tensile reaches a maximum from a very flat curve, but it does not obviate the disadvantage of poor reproducibility of tensile strength tests.

Modulus ratio appears to be as good as, or better than, any of the previous methods. Because of the nature of the curve for modulus *vs.* time of cure, it is unnecessary to use the modulus of the optimum cure. Therefore, a marked undercure and a marked overcure can be used—in this case, the ratio of the 15- to the 90-minute moduli, where both moduli are taken at 300 per cent elongation. An increase in the rate of cure is thus indicated by an increase in the modulus ratio.

RATE OF CURE

Table II shows the increase in rate of cure indices with increasing moisture content for the various series. These data are plotted in Figure 1 against the total moisture added to the batches. If the acceleration of the rate of cure were a function of the total water added to a batch, one would expect that these curves would at least be parallel. In an attempt to explain these differences, the results were replotted in Figure 2, the abscissa being changed to percentage moisture retained when the batch is finally removed from the mill.

TABLE II

EFFECT OF METHOD OF ADDING WATER ON MODULUS RATIO

Code No.	% Water added[a]	% Water retained[a]	Modulus (lb. per sq. in.) Av. M_{15}	Av. M_{90}	Av. MR
		Moisture added to carbon black			
1	0.0	0.0	238	1413	0.168
6	1.0	0.0	220	1377	0.160
8	3.0	0.0	272	1486	0.183
9	4.0	0.67	280	1428	0.196
2	6.0	0.83	347	1470	0.236
3	7.0	1.5	440	1470	0.299
4	8.0	1.9	483	1450	0.333
5	9.0	2.25	600	1497	0.401
13	10.0	2.42	673	1510	0.446
		Moisture added to mill rolls			
1	0.0	0.0	165	1410	0.125
4	1.0	0.375	205	1525	0.135
5	2.0	0.59	245	1540	0.155
6	3.0	1.20	357	1585	0.225
7	4.0	1.50	475	1595	0.298
8	5.0	1.54	545	1600	0.340
9	6.0	2.0	615	1655	0.372
10	7.0	2.0	605	1640	0.370
11	8.0	2.8	675	1660	0.406
12	9.0	3.0	675	1645	0.411
13	10.0	3.12	680	1580	0.430
		Raw polymer crumb soaked in water			
1	0.0	0.0	160	1380	0.116
5	1.6	0.0	180	1400	0.128
3	2.7	0.0	185	1370	0.135
2	3.5	0.0	180	1400	0.128
4 —	4.5	0.25	160	1335	0.120
6	5.6	0.83	190	1425	0.133

[a] Based on polymer

The curves of Figure 2 check more closely than those of Figure 1. Figure 2 seems to show that there is little acceleration of the rate of cure until the moisture retained exceeds 0.25 per cent. Between 0.25 and about 2 per cent there is a considerable increase in the rate of cure. If the data are plotted as the logarithm of modulus ratio against moisture retained, this region appears as a straight line, probably indicating chemical reaction during cure. Above 2 per cent moisture retained, the curves flatten, and thus show little further acceleration of the rate of cure. This region, however, is probably of little practical value, since there would be considerable danger of the stock blistering during cure.

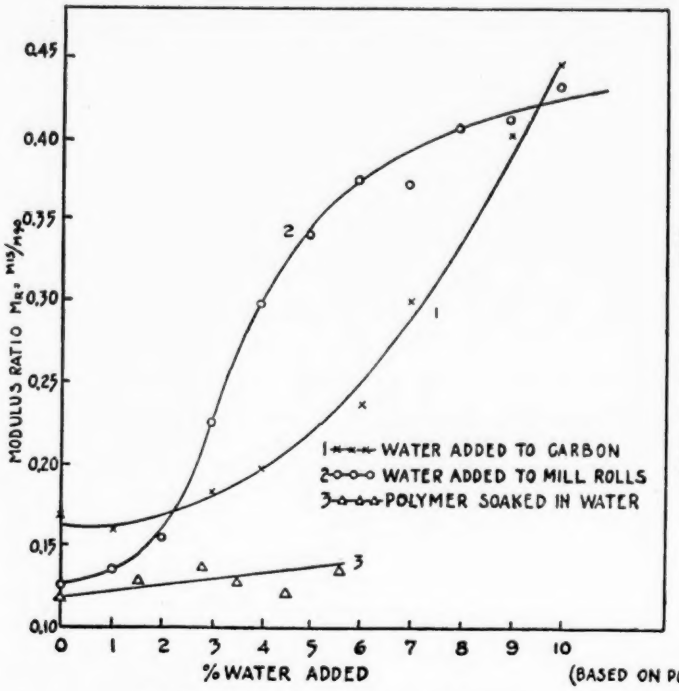

FIG. 1.—Effect of water added on modulus ratio.

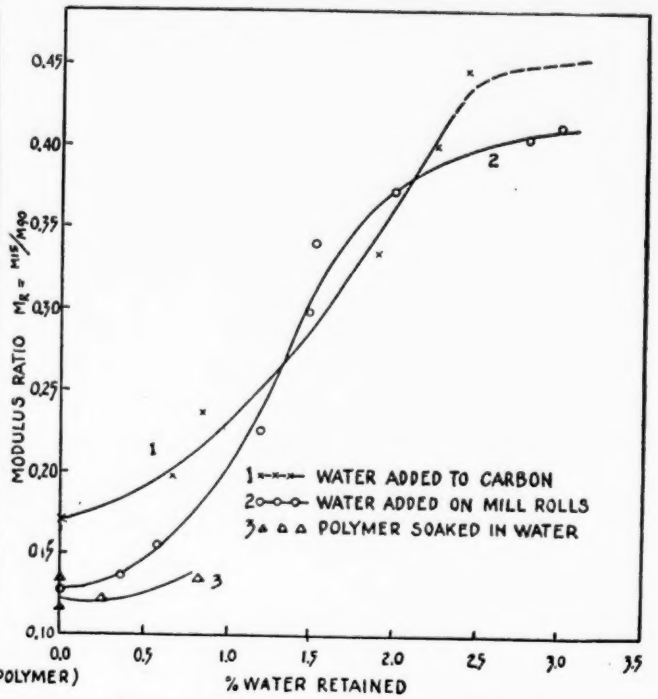

FIG. 2.—Modulus ratio as a function of water retained.

Curve 3, Figure 1, is a straight line and indicates a practically constant rate of cure. In Figure 2, however, this curve is so compressed that the experimental points appear to cover only the initial stage of slight acceleration; that is, most of the moisture added to the polymer in this manner is lost during milling. Since it was impossible to handle polymer with higher initial moisture contents than those shown, this curve could not be continued. It appears likely that, if this curve could be extended, it would show the same region of rapid acceleration as the other two curves.

The curves of Figure 3 show that the earlier the moisture is added in the mixing procedure, the lower the amount of water retained. The relatively

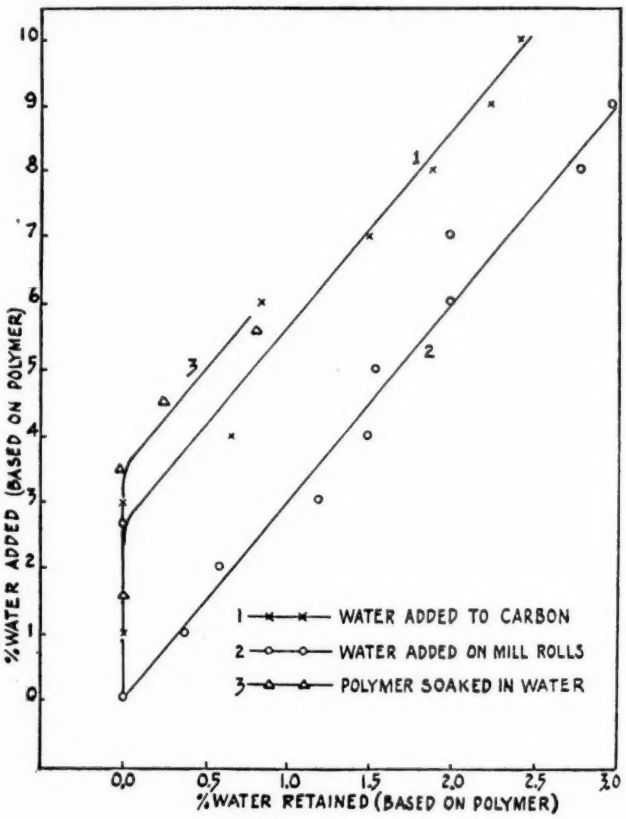

FIG. 3.—Relation between water added and water retained by a batch.

small difference between curves 1 and 3 and the large difference between curves 1 and 2 are explained by the rapid increase in the batch temperature when the carbon black is added. The ordinates at 0 per cent water retained for curves 1 and 3 are of particular interest. No moisture is retained, and thus there is no acceleration in the rate of cure until the carbon black contains 3 per cent moisture (on the polymer) or the polymer itself contains 3.5 per cent moisture. Since the maximum moisture content of carbon black as received is 2 per cent[1]

of the polymer weight and since the maximum moisture content of specification GR-S is 0.75 per cent, it appears that no moisture will be retained from either of these sources; therefore, neither source should contribute to variations in the rate of cure as far as moisture is concerned. These findings are in substantial agreement with others previously reported[3].

The calculation of water retained in the series where it was added to the carbon black is admittedly inaccurate since an error of 0.1 per cent in weighing would give an absolute error of 0.163 per cent in the calculated moisture retained. If the experimental values of percentage moisture retained for the series in which the moisture was added to the carbon black are corrected to curve 1, Figure 3, the curve for modulus ratio *vs.* water retained parallels more closely the curve for the moisture addition on the mill rolls and gives further evidence of a break above 2 per cent moisture retained.

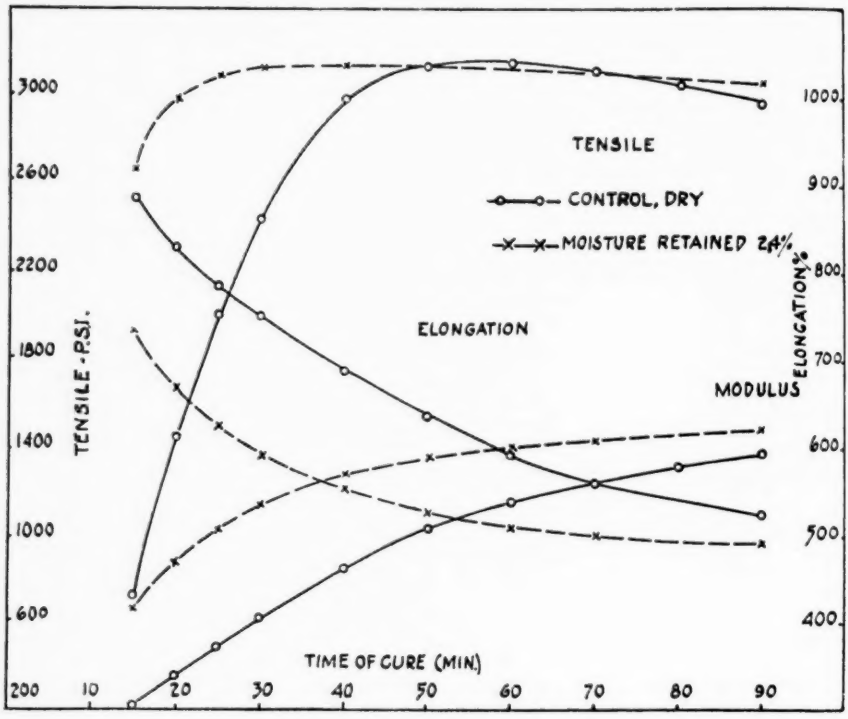

FIG. 4.—Comparison of curing curves.

Figure 4 shows typical curing curves for a normal dry batch and the same stock plus 2.4 per cent moisture retained. The different in the rate of cure is apparent.

Braendle and Wiegand's paper[1] on this subject shows a graph of percentage moisture in polymer against time to best cure, in which an increase in moisture content of GR-S polymer from 0.1 to 0.5 per cent is shown to decrease the time to best cure from 100 to 70 minutes at 280° F. Further, two-thirds of this difference, or 20-minute curing time, is shown to occur between moisture contents of 0.13 and 0.19 per cent. It seems unlikely that a difference of 0.06

per cent water could cause such a large variation in the rate of cure. Moreover, the entire moisture range of their graph is far below the minimum raw polymer moisture content which the present data show is necessary for any acceleration of the rate of cure. A study of the data used by these investigators reveals that they used polymers from three different sources. While GR-S from any one producing plant should have a uniform rate of cure, GR-S from different plants may not have. For example, GR-S coagulated with salt and acid contains up to 0.75 per cent sodium chloride, a known accelerator of cure. It is to be expected, therefore, that this material will curve faster than alum-coagulated GR-S, which contains no sodium chloride.

In the same paper the following statement appears: ". . . normally occurring amounts of moisture in carbon black are held so tightly that they do not effect cure". According to the data presented here, this water does not affect cure, not because it is held tightly by the carbon black, but because it is lost to the batch by evaporation.

EFFECT OF MOISTURE ON PHYSICAL PROPERTIES

To evaluate the effect of variation in moisture on physical properties, it is necessary to pick equivalent rates of cure. As a basis the point was chosen where the 300 per cent modulus equals 1200 pounds per square inch ($M_{300} = 1200$). Tensile strengths and elongations of various batches are compared at this point. The results (Table III) indicate no significant variation in physical properties with moisture content.

It has been reported[4] that in factory operation the addition of water to Banbury batches results in improved processing characteristics and physical

TABLE III

EFFECT OF MOISTURE ON PHYSICAL PROPERTIES OF GR-S

Code No.	% Moisture added[a]	% Moisture retained[a]	$TM_{300}=1200$, (lb. per sq. in.)	$EM_{300}=1200$, %
		Moisture incorporated through carbon black		
1	0.0	0.0	3150	575
6	1.0	0.0	3280	590
8	3.0	0.0	3275	595
9	4.0	0.67	3370	600
2	6.0	0.83	3390	590
3	7.0	1.5	3270	585
4	8.0	1.9	3280	590
5	9.0	2.25	3320	595
13	10.0	2.42	3145	580
		Moisture added on mill rolls		
1	0.0	0.0	3160	610
4	1.0	0.375	3290	605
5	2.0	0.59	3200	595
6	3.0	1.20	3310	595
7	4.0	1.50	3250	600
8	5.0	1.54	3180	590
9	6.0	2.0	3200	600
10	7.0	2.0	3160	585
11	8.0	2.8	3130	590
12	9.0	3.0	3240	590
13	10.0	3.12	3170	590

[a] Based on polymer

properties. This improvement is observed only when water is added after the compounding ingredients are in the batch. The probable explanation of this improvement is that water chills the Banbury batch and thereby reduces the heat deterioration of GR-S. Further, at the reduced temperature the stock is less plastic, more work is done on it, and physical properties are thus enhanced. This effect is probably secondary to the reduction in heat deterioration. Since laboratory mill-mixed batches are much cooler than Banbury batches mixed in the factory, it is not surprising that no improvement is noted in laboratory evaluations.

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ORGANIC ANALYSIS OF HEVEA LATEX VIII. DEVELOPMENT OF A GENERAL SCHEME OF ANALYSIS *

R. F. A. ALTMAN

VIJVERWEG 11, WASSENAAR, HOLLAND

1. INTRODUCTION

A thorough qualitative and quantitative knowledge of the nonrubber components of latex undoubtedly is of fundamental importance in connection with both theoretical and applied rubber chemistry. In studying various problems in this field, difficulties have often been encountered which might have been avoided if the chemical composition of the latex had been known. Theories which are aimed at explaining many obscure phenomena cannot be thoroughly tested unless it is known what components are present in latex and their concentration.

Moreover it is also worth while for purely practical considerations to do one's utmost to gather data on the nonrubber components, for, it has been repeatedly proved that these nonrubber components exert a considerable influence on various properties of rubber which are of practical importance, such as vulcanizing capacity, aging, plasticity, color, water absorption, etc[1].

Hence, it is no wonder that in the course of years a great deal of attention has been paid to the analytical chemical investigation of latex and crude rubber[2].

Results up to the present time are not in keeping with the amount of work which has been done, because of the fact that latex is a rather unmanageable material. In chemical investigations of the nonrubber components, the rubber hydrocarbon has invariably been an almost insuperable hindrance, because its elimination from the latex mixture has been effected only by adding a more or less strongly reacting substance (coagulant) which undoubtedly affects the original condition of the nonrubber components. The coagulation process has the additional disadvantage that these components are distributed more or less arbitrarily in the coagulum and in the serum[3].

Hence an investigation which deals with only one of these two products of coagulation must be incomplete[3], and for the reasons already explained the results cannot be simply interpolated in terms of fresh latex. The same holds true of analyses of ammoniated latex or of products prepared from it.

For this reason the quantitative separation of nonrubber components in their original condition is imperative for the complete and reliable analysis of Hevea latex. Yet the preparation of this ideal sample of analysis is not possible in practice, because untraceable chemical reactions take place within the latex immediately after it leaves the tree. The only alternative is to check these reactions as far as possible.

From the foregoing it will be clear that only fresh unammoniated latex can be considered to be a reliable starting material. As the composition of

* Reprinted from the *Archief voor de Rubbercultuur*, Vol. 25, pages 423 and following (1941).

latex depends on various factors, *viz.*, condition of the soil, climatological circumstances, individual properties of the trees, leaf-fall, sowing time, etc., analyses of any two latex samples generally show considerable deviations. Hence, to obtain fairly reproducible results, one has to start with clone latices, in which case it is advisable to choose only a few trees as latex-producers.

The choice of starting material may involve no difficulties, but the effective quantitative separation of the nonrubber components in their original state represent a more complicated problem. In any attempt to solve this problem, the low stability of latex as a biological mixture of several chemical substances must be borne in mind. As a matter of fact it is the daily task of the phytochemist to stop or to check as far as possible any chemical, bacterial or enzymic reactions which occur in such mixtures.

As is known, enzymic reactions can be prevented either by rapidly heating the material under investigation, or by the addition of strong alcohol. Neither method is practicable in the case of Hevea latex, since the rubber immediately coagulates, with resulting absorption of a considerable part of the nonrubber constituents by the coagulum, so that they are lost to the analytical investigation (see below). By heating, important chemical changes are bound to occur, and the use of alcohol[4] has the disadvantage that the enzyme-destroying action of this material fails to reach in time the interior of the solid and impenetrable rubber mass.

Rhodes and Bishop[5] described a method for the separation of the lipoids from latex. Latex is added in a thin stream to an excess of alcohol (two and one-half volumes). This thin stream coagulates in the alcohol as a spongy mass, which comes into an intimate contact with the solvent on account of its relatively large surface. A considerable portion of the nonrubber components is accordingly taken up by the solvent. Separation of the rubber and the nonrubber components is, however, still far from complete, as is proved, for example, by the fact that the coagulating spongy rubber retains at least 82 to 90 per cent of the ether-soluble substances occurring in the latex[6]. For the water-soluble components this percentage is possibly lower. Anyway the method of Rhodes and Bishop by no means approaches a quantitative separation of the nonrubber components in latex. The fact that the method can be completed and improved comparatively easily was pointed out in some of our previous publications[7].

Formerly we attempted only to separate a single group of compounds from the complex latex mixture, but the following deals with a method for analysis which makes possible the separation of several groups of organic compounds from the same latex sample.

2. PREPARATION OF A SAMPLE SUITABLE FOR ANALYSIS

According to the considerations mentioned above, the preparation of a suitable sample, *i.e.*, a mixture in which all components are rubber-free and in their original state, must meet the following conditions:

(1) unammoniated latex, as fresh as possible, and preferably clone latex, should be the material to start with;
(2) all chemical, bacterial or enzymic reactions likely to alter the original composition of the nonrubber components should be checked as far as possible;
(3) separation between rubber on the one hand and nonrubber components on the other must be complete.

The first condition can be easily fulfilled in the latex-producing countries. As to the other conditions, the following comments may be made.

In the previous paragraph we alluded to the impracticability of the Rhodes-Bishop method, at least in the original form, for our purpose. It appeared to fail to meet both requirements (2) and (3) above.

As regards bacterial and enzymic changes, it can be said that the less important they are the higher the final concentration of alcohol in the medium. In the experiment of Rhodes and Bishop this final concentration is ±75 per cent. This value can be increased considerably by using a larger excess of alcohol[8].

With regard to chemical changes, these depend on various circumstances, such as the composition of the mixture, temperature, acidity of the medium, etc. No alterations can be made in the composition of the mixture, so if compounds which may react together occur in the mixture, this reaction has to be checked or stopped. Consequently, besides maintaining a neutral reaction in the medium, the temperature should be kept as low as possible to prevent chemical changes.

Separation of the rubber and nonrubber components is the better, the more intensively the spongy rubber coagulum is extracted by the alcohol. This can be done by (1) enlarging the rubber surface; (2) using a large excess of solvent, and (3) raising the temperature of extraction.

A large rubber surface can be obtained in different ways. It has already been observed that the rubber coagulum in alcohol has a large surface on account of its spongy nature. By using a vigorous mechanical stirrer (by which the surface increases at the same time), this can be made fully profitable, for then the solvent makes contact with the coagulum more intensively. When the whole portion of latex is added, the coagulum on the bottom of the reaction vessel gradually loses its sponginess, and turns into a more or less compact mass. Consequently the large surface mentioned above is not stable. It is therefore efficient to crepe the coagulum as thinly as possible without washing, to roll this crepe in filter paper, and to extract the rolls.

Conditions (2) and (3) above can be fulfilled by various well known methods. Although on the one hand an elevated temperature is necessary for successful extraction, prevention of chemical reactions requires the lowest possible temperature. A compromise, inevitable in such a case, favors the extraction, since the aim is the *quantitive* separation of the nonrubber components. The fact that preservation of the aforesaid components is not attempted at any cost is motivated by the following considerations.

In the first place, for purely practical reasons all cumbrous precautions have been omitted to preserve the fresh latex as it flows from the tree. The interval between the commencement of tapping and the arrival of latex in the laboratory easily covers some hours, during which various changes take place in the material.

Secondly, it appears that the nonrubber components show such affinity for rubber that complete separation by a cold extraction is successful only if continued for some days or even weeks. As time and temperature exert the same influence on the reaction velocity, it makes little difference whether a short extraction is carried out at a high temperature or a very long one at a low temperature. Moreover the difference between the temperature concerned, *viz.*, the boiling point of alcohol (78° C) and room temperature in the tropics (30° C) is small.

Thirdly, a high extraction temperature has the advantage of accentuating

the enzyme-killing effect of the alcohol. The bacterial reactions which might still take place in a strong alcohol medium are in that case out of the question.

Finally we may point to the fact that the majority of investigators prefer to extract vegetable matter with boiling alcohol[9].

Since in our experiments chemical reactions did indeed take place[10], we had to restrict them to a minimum. Thus special attention had to be paid to keeping the reaction of the medium in which the rubber was to be extracted neutral, for an acid or alkaline reaction exerts an unfavorable influence on the original composition of the nonrubber components.

The reaction of the extracting liquid gradually becomes more acid as a consequence of phosphoric acid being liberated. However, by adding powdered calcium carbonate it appears possible to keep the reaction constantly neutral.

In the following a method for the preparation of a mixture suitable for the analysis of different groups of organic compounds is described. This scheme has been evolved from all the considerations and conclusions above and from other, earlier methods for the isolation of amino acids[7], amines, betaines[7], fat acids, resin acids, sterols and wax alcohols[6].

One liter of latex is poured in a thin stream with rapid mechanical stirring into nine liters of 96 per cent alcohol. The spongy coagulum which ordinarily forms settles on the bottom of the high-walled vessel, where it is kept slowly rotating by the stirrer. After latex is added, the rubber sponge is vigorously pressed out by hand. The alcoholic solution, which is faint yellow, is then sucked off from the precipitated fine particles, which appear to contain rubber, proteins and inorganic compounds, principally ammonium-magnesium phosphate. Meantime, the coagulum is creped thin, without using any wash water, the thin crepe is rolled in filter paper, into rolls 12–15 cm. long and about 3 cm. in diameter, which are extracted in either a large Soxhlet apparatus, or in a 5-liter round-bottom flask. The alcoholic solution recovered is used as the extracting liquid.

The Soxhlet extraction, which must be continued for 36–48 hours, may be best executed under reduced pressure so as to avoid as far as possible chemical decomposition of the extracted latex components. It is advisable to refresh the extracting liquid every 10–12 hours. In operating with a round-bottom flask, which is best placed in an oil bath, the extracting liquid, about every 3 hours, must necessarily be replaced by new quantities of either the alcoholic solution or fresh alcohol. Since strong acids, some of them identified as glycerophosphoric acids, are formed during extraction, some neutralizing agent, such as calcium carbonate, should be added.

The alcoholic extracts obtained, which are distinct yellow or orange, are then distilled under reduced pressure in carbon dioxide.

The distillation residues give a turbid liquid, in which the phosphatides form a buttery deposit. By thoroughly shaking three times with fresh ether, to which if necessary alcohol has been added, all ether-soluble substances can be separated quantitatively. The other nonrubber components of the latex are either in the water layer, or in the extracted rubber rolls. These rolls are again extracted three times for half an hour with $2\frac{1}{2}$ liters of water, each time at boiling temperature, to separate quantitatively the substances soluble in water. The aqueous extracts are evaporated *in vacuo* and added to the water layer obtained before.

These aqueous and ether extracts, which will be dealt with separately in the following sections, are a very suitable starting material for the separation of various groups of organic compounds.

ETHER EXTRACT

For the separation of the ether-soluble components, the ether extract obtained as described above is distilled, first under normal, then under reduced pressure, while carbon dioxide is led in. In this way a brown-yellow to orange-red paste is obtained, out of which the final drops of water cannot be isolated in the usual way[11]. It is dissolved in some absolute alcohol and redistilled *in vacuo*. This process, repeated if necessary, has proved to be an efficacious method of drying this kind of substances.

The distillation residue is taken up in dry ether, transferred quantitatively into a crystallyzing dish and, after careful evaporation of the ether, kept until constant weight in a vacuum-desiccator on blue gel.

The sample obtained is divided into three portions, which are analyzed separately:

(1) acid number, saponification number, nitrogen content, phosphorus content
(2) lecithins and cephalins
(3) fat acids, resin acids, sterols, wax-alcohols

The investigation of sample *1* needs no further discussion[12].

The lecithin and cephalin contents can be estimated by dissolving sample *2* in ether, filtering the insoluble parts[13] and pouring the filtrate into an excess of acetone[12]. Lecithins and cephalins precipitate, whereas fats, fat acids and other compounds remain in solution.

The precipitate is kept in a vacuum desiccator on blue gel, and is then extracted with hot alcohol. The lecithins dissolve whereas the cephalins are insoluble.

For brevity we refer to the procedure already described for the determination of the fat acid, resin acid, sterol and wax alcohol contents[6].

THE AQUEOUS EXTRACT

Different methods can be followed for a qualitative investigation of the aqueous solution, obtained as described in the section on the "Preparation of a Sample Suitable for Analysis." The usual specific reactions may be carried out on the different groups of organic compounds which will throw light on the composition of the mixture concerned. This information can be broadened considerably by separating the components, although it is far from quantitative when carried out by the lead precipitate method[14]. This method can be recommended at least for the first orientative investigation. Once having determined the groups of compounds in the mixture, their quantitative isolation requires a special procedure.

The procedure may be elucidated with a single example.

If in some way or another the presence of free amino acids in the mixture has been proved, a method for separating this group of compounds as completely as possible must be worked out[15]. A method for the isolation of amino acids has already been described[7]. The same method can be applied to the aqueous extract which, as a matter of fact, is an even more suitable sample for analysis than the liquid used formerly.

The remarks on amino acids also hold for the other groups of compounds present in the mixture, including amines, betaines, amides, sugars, quebrachitol, proteins, vegetable acids, etc. The greatest difficulty is to find the most suitable and specific method for the quantitative isolation of the separate groups of compounds.

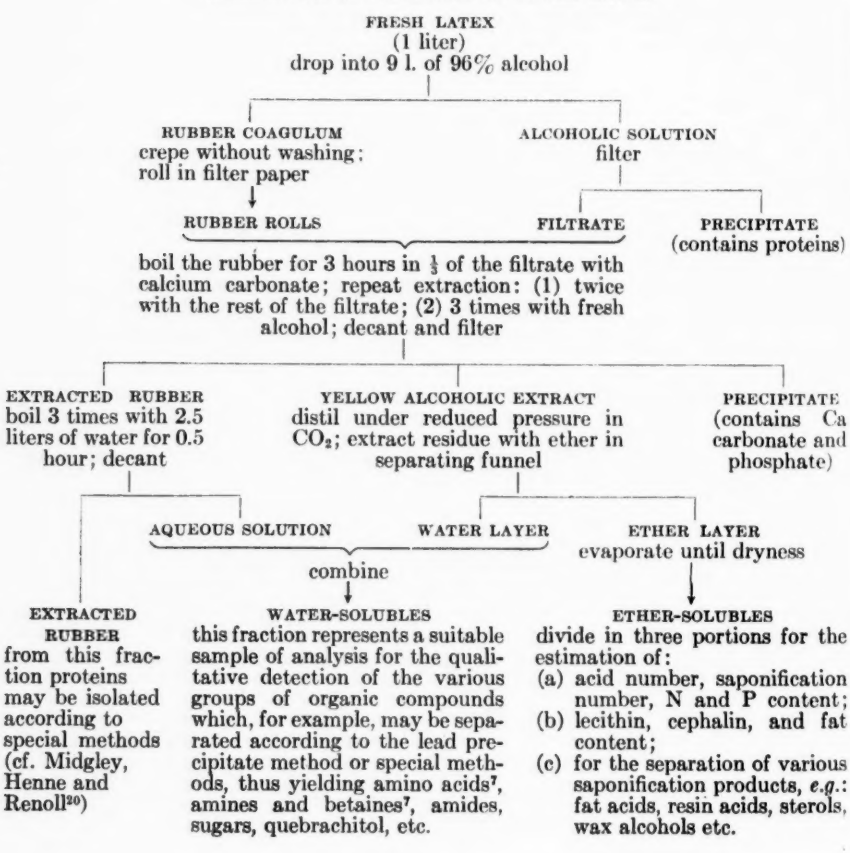
THE EXTRACTED RUBBER

The raw rubber initially extracted with alcohol and then with water appears to contain still other elements in addition to rubber hydrocarbon. If the rubber is extracted with acetone a sticky substance is found in the extract, which resembles "caoutchol"[16]. These are possibly oxidation products of rubber hydrocarbon[17]. The extracted rubber apparently contains also nitrogen, probably originating from the proteins precipitated in the rubber. The latter can be isolated, *e.g.*, by application of the method described by Midgley, Henne and Renoll[20].

DISCUSSION

Organic compounds in latex occur in such a multitude of different compositions that a complete analysis of the extremely complex mixture seems almost impossible. A thorough knowledge of the chemical composition of latex is, however, of such paramount importance that the study of this difficult problem of analysis deserves our full attention. Obviously this problem cannot be solved unless it is tackled in steps and at the same time systematically. An attempt in this direction was made by drawing up a scheme of analysis. It is

SCHEME FOR THE ANALYSIS OF HEVEA LATEX


FRESH LATEX
(1 liter)
drop into 9 l. of 96% alcohol
RUBBER COAGULUM
crepe without washing; roll in filter paper
ALCOHOLIC SOLUTION
filter
RUBBER ROLLS
FILTRATE
PRECIPITATE
(contains proteins)
boil the rubber for 3 hours in ⅓ of the filtrate with calcium carbonate; repeat extraction: (1) twice with the rest of the filtrate; (2) 3 times with fresh alcohol; decant and filter
EXTRACTED RUBBER
boil 3 times with 2.5 liters of water for 0.5 hour; decant
YELLOW ALCOHOLIC EXTRACT
distil under reduced pressure in CO_2; extract residue with ether in separating funnel
PRECIPITATE
(contains Ca carbonate and phosphate)
AQUEOUS SOLUTION
WATER LAYER
ETHER LAYER
evaporate until dryness
combine
EXTRACTED RUBBER
from this fraction proteins may be isolated according to special methods (cf. Midgley, Henne and Renoll[20])
WATER-SOLUBLES
this fraction represents a suitable sample of analysis for the qualitative detection of the various groups of organic compounds which, for example, may be separated according to the lead precipitate method or special methods, thus yielding amino acids[7], amines and betaines[7], amides, sugars, quebrachitol, etc.
ETHER-SOLUBLES
divide in three portions for the estimation of:
(a) acid number, saponification number, N and P content;
(b) lecithin, cephalin, and fat content;
(c) for the separation of various saponification products, *e.g.*: fat acids, resin acids, sterols, wax alcohols etc.

intended to carry this scheme into effect step by step. In doing this we are well aware of the fact that the scheme is far from perfect, that the process, which has been started meantime[18] will be a protracted affair, and that the elaboration of the scheme will encounter many difficulties, which may even prove insuperable. It goes without saying, that any better scheme will be welcomed, and every trial of our scheme for its practicability[19] will meet appreciation on our part.

SUMMARY

An attempt is made in this work to show the desirability and the practicability of a complete analysis of Hevea latex. It has been found that fresh, unammoniated latex is the only trustworthy starting material for analysis. Difficulties encountered in the analysis are due principally to (1) the troublesome property of the rubber hydrocarbon to adsorb, and hold firmly, the other components of latex; (2) probable chemical, enzymic, and bacterial changes, which cause great difficulties in the isolation of those components in the state in which they are originally present in latex, and (3) the lack of proven methods of quantitative separation of the various groups of organic compounds.

In his attempt at an ideal method of analysis, the author, due to the above-named difficulties, is faced with the apparent impossibility, as yet, of separating the various components of latex quantitatively and in the original state in which they are present in the latex. As a result of much theoretical consideration and practical experience, gained meantime, the author has reached a method, the scheme of which is described in the present work.

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[3] In this connection, as has already been pointed out, our investigations of proteins (cf. Altman, *Arch. Rubbercultuur* **23**, 239 (1939); **24**, 431 (1940); RUBBER CHEM. TECH. **13**, 505 (1940); **14**, 300 (1941)) and lecithins (cf. Altman and Kraay, *Arch. Rubbercultuur* **24**, 58 (1940); RUBBER CHEM. TECH. **13**, 750 (1940); *Rec. trav. chim.* **59**, 877 (1940)) must be regarded as incomplete.
[4] The use of other enzyme poisons (potassium cyanide, mercuric chloride, etc.) should be strictly avoided, because they bring about various chemical changes in latex. Furthermore the addition of chemicals to the already very complex latex mixture increases the difficulty of handling it.
[5] Rhodes and Bishop, *Quart. J. Rubber Inst. Malaya* **2**, 125 (1930).
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[7] Altman, *Arch. Rubbercultuur* **24**, 647 (1940); **25**, 1 (1941); RUBBER CHEM. TECH. **14**, 659 (1941).
[8] If, for example, 9 parts of alcohol are mixed with 1 part of latex, the final concentration is about 90 per cent. The use of absolute alcohol increases this concentration still more.
[9] Stas, Dragendorff, Otto, Rosenthaler, Zellner and others, in Klein, "Handbuch der Pflanzeranalyse", Vienna, **1931**, Vol. 1, pp. 585 and following.
[10] It is known that glycoside compounds decompose at the boiling temperature of alcohol.
[11] Drying of the ether solution by sodium sulfate or other dehydrating agent appears to be unsuitable because of the large quantities of alcohol in the extract.
[12] Altman and Kraay, *Arch. Rubbercultuur* **24**, 58 (1940); RUBBER CHEM. TECH. **13**, 750 (1940); *Rec. trav. chim.* **59**, 877 (1940).
[13] These insoluble substances, which appear always to be present, have been identified as a sterolide.
[14] See Klein, "Handbuch der Pflanzenanalyse", Vienna, **1931**, Vol. 1, p. 593.
[15] A truly quantitative separation is, as is known, a rare accomplishment in organic analysis.
[16] Kraay and Altman, *Arch. Rubbercultuur* **22**, 223, 231 (1938); RUBBER CHEM. TECH. **13**, 124 (1940).
[17] An investigation of these substances is in progress.
[18] Altman, *Arch. Rubbercultuur* **24**, 647 (1940); **25**, 1, 142 (1941); RUBBER CHEM. TECH. **14**, 659 (1941).
[19] Its utility has not yet been fully proved by our own experiments.
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ORGANIC ANALYSIS OF HEVEA LATEX. VII. FAT ACIDS, RESIN ACIDS, STEROLS, AND WAX ALCOHOLS. A PRELIMINARY NOTE *

R. F. A. ALTMAN

VIJVERWEG 11, WASSENAAR, HOLLAND

INTRODUCTION

In this note the isolation of the ether-soluble nonrubber components of latex will be described. As far as feasible, a quantative separation of the fat acids, resin acids, sterols, and wax-alcohols was attempted.

METHOD FOR THE ISOLATION OF NONVOLATILE FAT ACIDS, RESIN ACIDS, STEROLS, AND WAX ALCOHOLS FROM FRESH LATEX

One liter of latex is poured slowly with rapid mechanical stirring, from a dropping funnel into 7.5 liters of 96 per cent alcohol[1] at room temperature. The rubber coagulum is removed from the alcohol by tweezers and placed on a Büchner funnel. While the coagulum is creped very thin without using any wash water, the alcoholic solution is sucked off from the precipitated proteins. The crepe is then rolled in filter paper and refluxed for 3 hours with one-half of the clear alcoholic solution. To the mass 10 grams of calcium carbonate is added. In this way a distinctly yellow alcoholic extract is obtained, which is decanted from the rubber rolls and filtered from the calcium carbonate, the latter being partly converted into calcium phosphate. The alcoholic extract is then distilled under reduced pressure in carbon dioxide. Meantime the rubber rolls are again boiled 3 hours with the second half of the alcoholic solution; this yields a second portion of the yellow extract to be concentrated. The distillation residues yield, when shaken three times with pure ether in a separating funnel, with the addition of a small quantity of alcohol, a brownish water layer, and a yellow to orange ether layer. The latter, when evaporated to dryness, yields a yellow-orange buttery substance, containing the desired mixture of fat acids, resin acids, sterols, and wax alcohols. Depending on the latex used, the yield of this buttery mass varies considerably. From the five latex samples under investigation the following yields in grams per liter of latex were obtained: 8.83; 9.26; 8.52; 8.14, and 13.84.

ANALYSIS OF THE ETHER-SOLUBLE FRACTION

The buttery mixture obtained (100 per cent) is subjected to a cold saponification process according to Henriques[2] by dissolving it in 8 to 10 volumes of ligroin, with a large excess of 1 *N* alcoholic potash solution. Saponification is completed by leaving the reaction mass for 24 hours at room temperature. The ligroin and alcohol are then distilled, preferably *in vacuo*. The distillation

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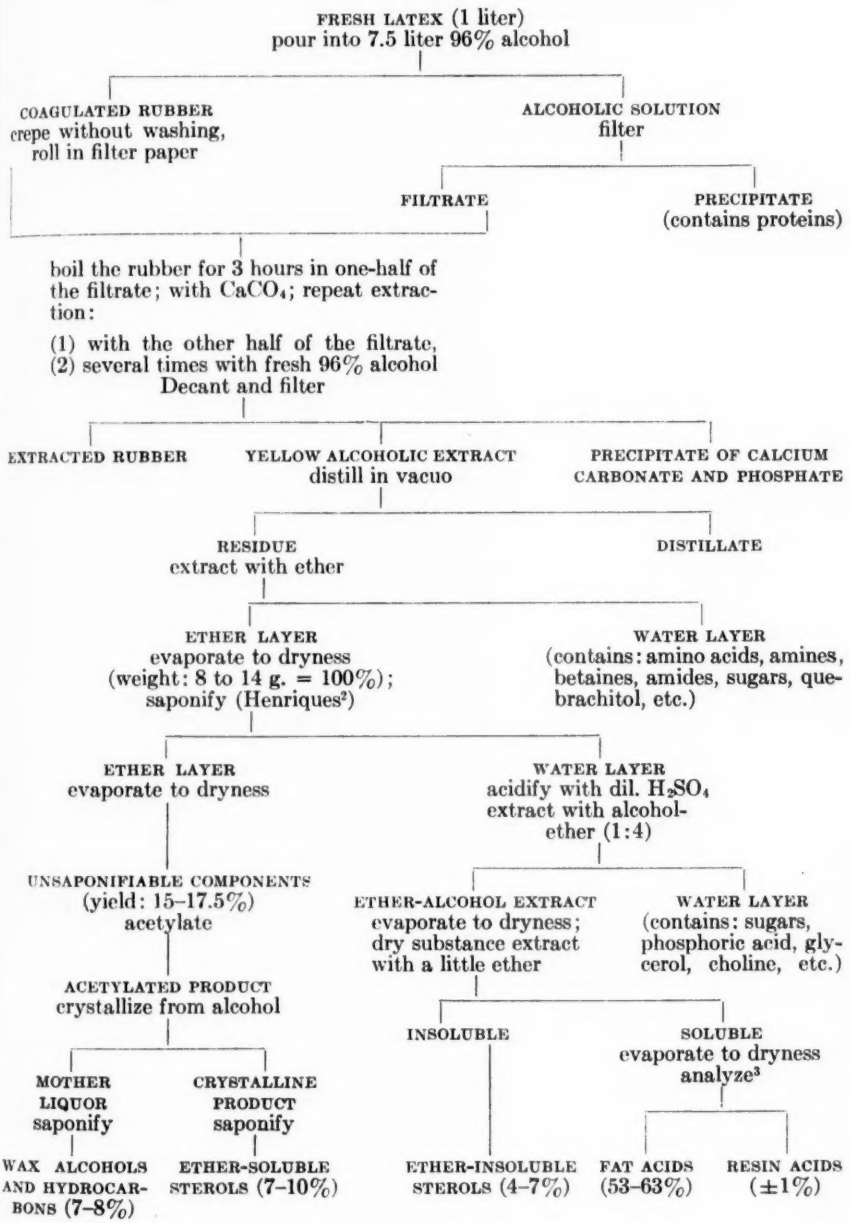
residue is taken up with water and repeatedly extracted with ether. Whereas the ether layer contains the unsaponifiables, in the water layer the potassium salts of the fat acids and resin acids are dissolved. These acids are isolated by

SCHEME OF THE METHOD ADOPTED FOR THE ISOLATION OF NONVOLATILE FAT ACIDS, RESIN ACIDS, STEROLS, WAX ALCOHOLS AND HYDROCARBONS



acidifying with dilute sulfuric acid and extracting with an alcohol-ether mixture (1:4). This second water layer appeared to contain phosphoric acid, glycerol, choline and sugars.

The ether-alcohol solution, evaporated to dryness, yields a brown oily residue, from which, by digesting with a small quantity of ether, an insoluble substance is obtained (yield: 4–7 per cent). It gives the reactions of *sterols*. The remaining oil (yield: 4–7 per cent), consisting principally of *fat acids*, also contains resin acids which could be detected by means of the reactions of Liebermann-Storch-Morawski[3], Halphen[4], and Schapiro[5]. The acid number of the oil has an average value of 181. This is in good accord with the assumption that the mixture contains chiefly fat acids.

When the average molecular weight of the fat acids[6], which for the greater part are monobasic, is estimated at 282, one gram of KOH is equivalent to 5.03 mg. of fat acid. From 9.26 grams of the ether-soluble fraction 4.77 grams of the oily acid mixture was obtained. According to the acid number, this mixture contains $4.77 \times 181 \times 5.03$ mg. or 4.343 grams of fat acids.

The *resin acids* are separated according to the method of Twitchell[7] by saturating the alcoholic solution of the oil with dry hydrogen chloride gas at room temperature and leaving the reaction mixture for one hour. The mixture is then poured into five volumes of water, and shaken with low-boiling ligroin. The ligroin solution is washed with water and extracted once or twice with a solution containing 0.5 gram of potassium hydroxide, 45 cc. of water, and 5 cc. of alcohol. Only the resin acids dissolve, since the fat acids, being completely esterified, remain in the ligroin layer. The potassium salts of the resin acids are then decomposed with hydrocloric acid and taken up with ether. The ether solution is dried on anhydrous sodium sulfate, after which the ether is evaporated and the residue weighed. The resin acids are thus obtained in the form of a light brown partly crystalline substance (yield: about 1 per cent).

The unsaponifiables (see above) are analyzed as follows. The ether solution when evaporated to dryness yields a yellow to orange-red crystalline mass (15–17.5 per cent of the ether-soluble fraction), which is acetylated by boiling it with acetic anhydride for two hours. The boiling mass remains only slightly cloudy, indicating that only minute amounts of hydrocarbons are present. On cooling, a crystalline cake is obtained, to which water is added to decompose the excess acetic anhydride. The acetylated alcohols (sterols, wax alcohols) are then separated by extracting the mixture with ether, washing the ether layer successively with water and a dilute solution of sodium bicarbonate, drying the ether solution on anhydrous sodium sulfate, and evaporating the ether. The residue is now boiled with a small quantity of 96 per cent alcohol, in which the acetylated wax alcohols and the hydrocarbons dissolve completely; the acetylated sterols on the contrary are only partly soluble in boiling alcohol[7], and are insoluble in cold alcohol. The alcoholic solution is, therefore, cooled and sucked from the separating crystals of acetylated sterols, which are washed with ice-cold alcohol. In this way a reasonably satisfactory separation of the compounds mentioned is attained

The *sterols* are obtained in a free state by saponifying the crystals obtained with alcoholic potash, shaking the mixture with ether, and evaporating the ether. The yield of the separated pale yellow crystals amounts to 7 to 10 per cent. The reactions of sterols of Salkowsky, Liebermann-Burchardt, Mach and Tschugajew[9] give positive results. A remarkable fact is that only a relatively small portion of the sterol-mixture can be precipitated with alcoholic digitonin. The yield of the sterols isolated by means of digitonin amounts to only 2 per cent of the ether-soluble latex fraction.

The free *wax alcohols* are obtained from the acetylated product in the usual way as a light brown waxlike substance (yield: 7–8 per cent). This mixture, still containing the *hydrocarbons*, emits a weak but decided odor of flowers, which is probably due to decomposition products (ionone) of carotene originally present in latex[10].

Summarizing, it may be concluded from the discussion above that in one liter of fresh latex 8 to 14 grams of ether-soluble nonrubber components are present. This mixture when saponified yields 53–63 per cent of fat acids, about 1 per cent of resin acids, 11–15 per cent of sterols and 7–8 per cent of wax alcohols contaminated with hydrocarbons.

For reasons mentioned earlier[11] special attention is called to the high fat acid content. The percentage indicates the presence of about 4 to 9 grams of fat acids per liter of fresh latex, a value that is far higher than that found by Rhodes and Bishop[12], *viz.*, 1.4 grams per liter of latex[6].

Finally, attention is drawn to the fact that the investigation does not deal with the volatile components of latex.

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[6] Altman, and Kraay, *Arch. Rubbercultuur* **24**, 58 (1940); RUBBER CHEM. TECH. **13**, 750 (1940); *Rec. trav. chim.* **59**, 877 (1940).
[7] See Van Leent, "Analyse en Warkenkennis der Voornaamste Vette Lichamen", Amsterdam, **1934**, p. 143.
[8] Klein, "Handbuch der Pflanzenanalyse", Vienna, **1932**, Vol. 2, p. 623.
[9] See Dalmer, in Klein, "Handbuch der Pflanzenanalyse", Vienna **1932**, p. 712; Altman and Kraay, *Arch. Rubbercultuur* **24**, 69 (1940); RUBBER CHEM. TECH. **13**, 750 (1940); *Rec. trav. chim.* **59**, 877 (1940).
[10] Eaton and Fullerton, *Quart. J. Rubber Inst. Malaya* **1**, 135 (1929).
[11] Altman and Kraay, *Arch. Rubbercultuur* **24**, 71 (1940); RUBBER CHEM. TECH. **13**, 750 (1940); *Rec. trav. chim.* **59**, 877 (1940).
[12] Rhodes and Bishop, *Quart. J. Rubber Inst. Malaya* **2**, 125 (1930).

RECENT ADVANCES IN RUBBER ANALYSIS *

W. C. WAKE

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

This paper is limited to advances in those problems which the advent of synthetic rubbers has brought to the rubber analyst; that is, methods of analysis which serve to determine what rubber is, or what rubbers are present, and in what amount.

In the consideration of analytical problems it is convenient to assume what is in fact rarely true, that the nature of the sample to be examined gives no clue as to the polymer present. It is unlikely that an oil sealing ring or Jerrican washer will nowadays be made of, for example, natural rubber; the feel of a specimen, its spring or snap, as well as the use to which it is put, will give information to the rubber technologist. In the discussion, however, it must be assumed that the hypothetical specimen is of the wrong shape and size for the usual evaluation of physical properties, and of unknown purpose and make.

There have been, both here and in America, a number of papers published on the subject, and these will be referred to at appropriate places in the text; but there have been remarkably few reviews of the whole problem. The first was the official booklet published by the Ministry of Supply in their series for the Services Rubber Investigations[1]. It will be referred to in abbreviated form throughout this paper as U.9. Although officially limited in circulation, it is, by now, well known as containing the first systematic scheme for the identification and analysis of synthetic rubber. It will probably be superseded in the near future, but will remain the foundation of subsequent analytical schemes. The earliest review of the newer methods in the English technical press was by Stern[2], who dealt largely with identification; quantitative determination was left, in general, to the orthodox difference method, except in the case of natural rubber for which he gave details of its direct determination by oxidation to acetic acid.

A note with special emphasis on deciding whether specifications are met is given by Wyatt[3]. Where complete analysis of the compound is required also, all the data for application of the difference method are available, and it should not be neglected. Since the publication of U.9 and of Stern's article, new materials have become available for which modifications in the methods or interpretation of some tests are necessary; some new methods have been published; and work has been carried out on the subject in the laboratories of the Research Association of British Rubber Manufacturers. Detection and estimation of individual rubbers will be first reviewed, then more general methods, such as those based on unsaturation, and finally the place of specific reactions in the general scheme of analysis will be indicated.

Detection and Estimation of Natural Rubber.—The real use of the Weber color reaction for natural rubber came only when there was a possibility of a

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 21, No. 3, pages 158–174, October 1945.

material, apparently like natural rubber, but, in fact, some other polymer. Hence, after its mention by Weber[4] little attention has been paid to it until recently. The test is crude and there are several ways of carrying it out. Rubber, whether raw or vulcanized, is brominated with elemental bromine without dissolution of the rubber, and then warmed with phenol. A violet color develops. The present author, in conjunction with Parker[5] has shown that bromination must occur in the α-methylene position, since the product of addition of bromine at the double bond with no substitution fails to give any color when warmed with phenol, whereas the use of *N*-bromosuccinimide to substitute in the methylene group[6] readily gives the familiar color. The methylene group next to the double bond must be sufficiently reactive to lose a proton easily, for under the conditions employed, substitution in the allyl position is not normally possible. In natural rubber this activation is achieved by the methyl group, and hence, in general, the grouping $-CH_2-(CH_3)=C<$ is necessary, although other activation of the methylene group may suffice. The rubber chemist is concerned when substances other than natural rubber give the reaction, and this will occur whenever the above group is present in the polymer chain; that is, in any polyisoprene, or a copolymer containing isoprene, as is apparently the case with Neoprene-FR. The test had, therefore, no sooner become of real use than other factors arose which lessened its worth. When a positive result is obtained with the Weber reaction it may be taken that isoprene residues are almost certainly present but not necessarily as natural rubber.

A second color test is quoted by Dawson and Porritt[7] as specific for natural rubber. In this the rubber is (1) fused with trichloroacetic acid, giving a yellow-red coloration; (2) the resultant melt is then heated to the boiling point of the acid, the color darkening to orange-red; and (3) the melt is dissolved in water, giving a violet-gray precipitate. This has been verified on vulcanized rubber as well as smoked sheet, and also on a raw synthetic copolymer containing some 75 per cent of isoprene. The color is, therefore, unlikely to be due to natural impurities in the rubber or to compounding ingredients. A few other vulcanized and unvulcanized rubbers have been examined, with the results shown in Table 1, the stages (1), (2) and (3) being as above.

TABLE 1

THE TRICHLORACETIC TEST FOR RUBBER

	(1)	(2)	(3)
Natural rubber Alkali reclaim	Yellow-red Dirty-brown	Orange-red Black	Violet-gray ppt. Black ppt.
Neoprene-FR GR-S Butyl	Yellow	Brown	Yellow solution with faint ppt.

This test thus provides a check on the Weber reaction and conveniently eliminates Neoprene-FR. The degree of sensitivity has not been investigated, or the effect of other materials, but no trouble is anticipated from them. It should be pointed out that care needs to be taken when carbon black is present; the black may readily disperse into the melt, but the color can often be seen before this occurs. In the case of alkali reclaims, or in vulcanizates containing reclaim, it does not seem possible to prevent immediate dispersion of black, and this behavior may prove to be characteristic of this material.

The detection of natural rubber by means of its phosphorus content was suggested by Barnes, Williams, Davies and Gieseck[8]. Actually this method

was used independently at Croydon in 1943 in a confidential problem which involved distinguishing between natural rubber and a possible synthetic polyisoprene. It is, however, part of a general method which includes some synthetic rubbers, and will be dealt with more fully below.

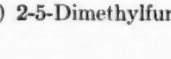
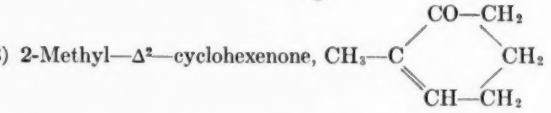
The direct estimation of natural rubber has become of great importance, since the possibility of other polymers present makes indirect methods hazardous if a full qualitative analysis has not been made. Also, in mixtures of natural rubber and GR-S, or other synthetic rubbers except those containing chlorine, the total rubbers can be estimated by difference, or by iodine value; then if one of the rubbers is estimated directly, the other can be calculated. When this procedure is adopted it is, on balance, preferable to estimate the natural rubber directly and the GR-S by calculation rather than *vice versa*.

The method recommended for natural rubber in U.9 is based on the methyl group determination of Kuhn and L'Orsa[9]. In this method, wet combustion of the substance by a chromic acid-sulfuric acid mixture proceeds as far as the acetic acid stage, the latter being removed by steam distillation and titrated. With various types of organic compounds, differing yields, expressed as fractions of a gram-mole of acetic acid per gram-mole of methyl groups, are obtained. Different types of compound give different yields, and to determine the methyl groups present it is usual to compare the yield obtained with some reference compound.

Values obtained in some recent work by Barthel and La Forge[10] are given as the first three compounds in Table 2.

TABLE 2

YIELD IN ESTIMATING METHYL GROUPS OF REFERENCE COMPOUNDS

Compound	Yield
(1) Crotonic acid, $CH_3 \cdot CH{=}CH \cdot COOH$	0.96
(2) 2-5-Dimethylfurane, 	0.85
(3) 2-Methyl—Δ^2—cyclohexenone, 	0.80
(4) Natural rubber, $—CH_2—C(CH_3){=}CH—CH_2—$	0.75
(5) Methyl rubber, $—CH_2—C(CH_3){=}C(CH_3)—CH_2—$	0.75

2-Methyl-Δ^2-cyclohexenone is obtained by oxidation of 1-methylcyclohexene with chromic acid[11] and from the close analogy existing between rubber and methyl cyclohexene it is, perhaps, permissible to assume that a preliminary stage in the oxidation of rubber involves oxidation of the methylene group to carbonyl. Hence, again by analogy, the yield of acetic acid comparable to that given by compound (3) would be expected; that is, 0.80. In fact, the literature[12] reports 0.75, the figure which is, it is believed, used generally both here and in America.

This value of 0.75 for natural rubber means that 3 moles of acetic acid are obtained for every 4 isoprene residues. This could be due either to loss of some of the acetic acid by further oxidation to carbon dioxide, or to the way the reaction takes place, kinetically speaking. The latter seems more probable, since sodium acetate, when treated under identical conditions, gives more

or less quantitative amounts of acetic acid, and also variation in the conditions of reaction with rubber can give yields of acetic acid considerably over 75 per cent. Yields varying between 90 and 99 per cent have been obtained by controlling the rate of oxidation, but, unfortunately, the control has not yet been stabilized to give as consistent results as are obtained by the orthodox procedure. All subsequent results and remarks relate to the standard procedure and apparatus given in U.9.

Sulfur combined with the rubber interferes, in some way at present unknown, with the reaction, and in its presence a correction is usually necessary. The results obtained with high-sulfur rubbers and ebonite indicate that, as a reasonable approximation, for each three atoms of combined sulfur, two isoprene residues no longer yield acetic acid, *i.e.*, 1.5 moles of acetic acid are lost. This is shown in Figure 1, in which the gram-mole of rubber hydrocarbon

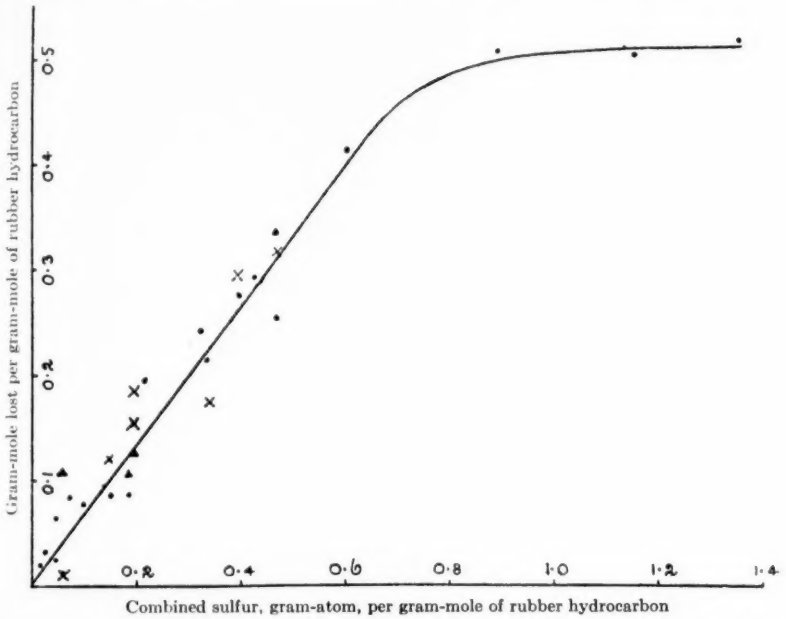


FIG. 1.—(Rubber hydrocarbon estimation by oxidation method ●, iodine value ×, bromine value ▲).

apparently lost is plotted against gram-atoms of combined sulfur. The line is that for exactly two isoprene residues lost per three atoms of sulfur combined, and it will be seen that it is the best fit for the points obtained from the oxidation method. The curve is also a good fit for the few points available, in which the rubber hydrocarbon lost was measured by the loss of unsaturation to iodine and bromine. This is of twofold interest, for any theory of vulcanization must account for the integral relationship of two isoprenes to three sulfurs, and an integral relationship would be expected if the number of types of reaction occurring in vulcanization were small. Secondly, it suggests that the failure of certain isoprene units to give acetic acid on oxidation is connected with the loss of unsaturation. It means also that the same correction for combined sulfur can be used for all three types of estimation. This correction is given in Figure 2.

As will be noted, the correction for normal soft vulcanizates, containing but little sulfur is small and, in view of the accuracy normally attained in the rubber hydrocarbon estimation, the correction is not worth applying when the combined sulfur is less than 2.0 per cent of the rubber apparently present. The list of interfering substances and the effect of other rubbers on the determination, which is given in Table 7 of U.9, requires the addition of Neoprene-FR; this material is equivalent to 12 per cent of its weight of rubber hydrocarbon. Protein, if present in any quantity, will cause an error which cannot be eliminated because the protein cannot be extracted. This error is likely to occur in mixtures of rubber with leather.

As no survey since that of Burger, Donaldson and Baty[13] has been published giving the magnitude of the error likely in this estimation, it is worth

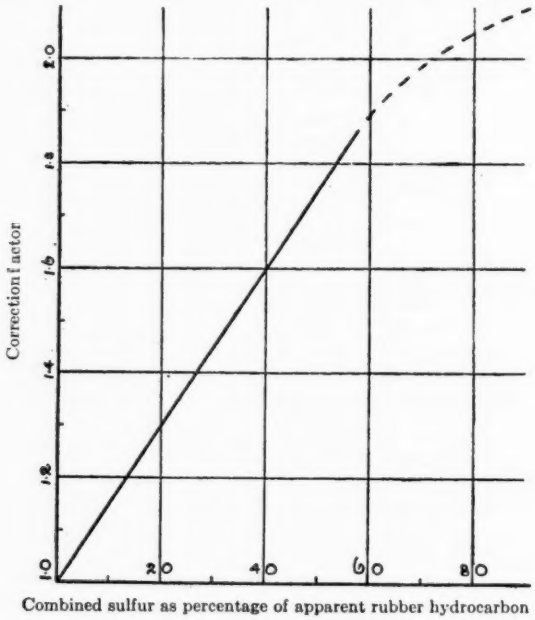


FIG. 2.

recording the experience at the laboratories of the Research Association of British Rubber Manufacturers. The mean deviation of the mean of duplicates, calculated on the assumption that the mix formulas are correct, is 1.55 for 15 results, which is equivalent to an estimated standard deviation of about 2.0 per cent. This suggests that one result in twenty will be in error by 4 per cent or more. Alternatively, if it is assumed that the rubber hydrocarbon obtained by the difference method is correct, the same result is obtained.

This can also be expressed that, in general, differences, between means of duplicates, of not less than 4 per cent are required before they can be said to be significant. The results from which these estimations of error are made are given in Table 3. The rubber hydrocarbon content of smoked sheets is taken as 93 per cent, following Van Rossem[14].

Reclaimed Natural Rubbers.—The direct estimation by oxidation for any type of reclaim is straightforward, except that the correction for combined

TABLE 3

ERRORS IN ESTIMATION OF RUBBER HYDROCARBON
(Based on means of duplicates)

Mix	From mix formula	By difference	Direct
1	47.8	46.9	47.3
2	47.7	47.7	46.9
3	47.5	48.1	46.0
4	47.4	46.6	46.1
5	48.0	—	49.1
6	48.2	—	48.5
7 u.	56.1	59.5	58.5
7 v.	56.1	54.6	59.0
8	71.0	74.6	74.0
9	44.8	50.8	46.2
10	46.3	45.6	44.4
11	46.2	45.7	47.0
12	46.2	45.7	44.6
13	46.0	45.5	44.5
14	45.8	45.6	44.6

7 u.: unvulcanized; 7 v.: vulcanized.

sulfur is likely to be more important. Newton[15] pointed out that a part of the rubber hydrocarbon in reclaim was not available for vulcanization, and it was probable that it was the same part (combined with sulfur) which did not give acetic acid on oxidation. Therefore, conventional difference methods give all rubber present, whereas the oxidation method estimates that available for revulcanization. Hence, results by the direct method are always low unless a correction is made for the combined sulfur present. It is suggested, however, that in evaluating reclaim it is advantageous to accept the figure obtained without the sulfur correction as giving a better guide to the value of the reclaim.

Estimation of Unsaturation.—Methods based on unsaturation received an impetus from the paper of Kemp and Peters[16]. Since its publication, a number of determinations have been carried out and have shown that the method is capable of yielding good results. The foundation, and yet the stumbling block, of all methods based on unsaturation is the necessity for the dissolution of the vulcanized material before the estimation can be attempted. Inefficient dissolution of the rubber has been found the most probable source of error, and a procedure slightly modified from that of Kemp and Peters has been found preferable, of which full details are here recorded. The vulcanized sample is comminuted by buffing, and a weighed quantity of about 0.06 gram is acetone-extracted and then transferred without drying into 10 cc. of carbon tetrachloride. This mixture is heated on a hot plate in the fume cupboard, the carbon tetrachloride being boiled vigorously until the greater part of it has evaporated. By this time (a matter of 10 minutes or so) the rubber is well swollen and 50 grams of *p*-dichlorobenzene is added to the hot mixture, and heating (at approximately 180° C) is continued until the sample is completely dissolved. This procedure has been found to facilitate solution of the vulcanized rubbers, particularly GR-S, the complete solution of which usually takes a few hours. When dissolved, the mixture is allowed to cool and 50 cc. of chloroform is added just before crystallization is complete. This is followed by 25 cc. of 0.2 *N* iodine chloride solution in carbon tetrachloride. It is convenient to carry out the whole of the above procedure in an iodine flask which can be sealed against loss of reagent (iodine chloride) by a 15 per cent aqueous

solution of potassium iodide. After the addition of the iodine chloride and the sealing, it is allowed to stand in darkness for one hour at room temperature. The excess iodine chloride is estimated by washing in the potassium iodide solution from the seal, adding a further 25 cc. of this solution, 75 cc. of alcohol and, lastly, 40 cc. of water. Titration of the liberated iodine is performed in the usual way. The emulsion which is first formed breaks just before the end point, any carbon black present going into the organic solvent layer.

The method can be applied equally well to natural rubber, including reclaim, GR-S, and mixtures of these. Chloroprene and its copolymers will not react fully with iodine chloride, and they cannot be estimated by this method. Also, of course, these latter rubbers in mixtures cause interference, as some reaction does occur. Table 4 shows that good agreement with the iodine values published by Kemp and Peters[16] for raw materials has been obtained.

TABLE 4

IODINE VALUES OF SOME UNVULCANIZED RUBBERS

Rubber	Iodine value	Equivalent iodine value for pure hydrocarbon	Iodine value for pure hydrocarbon (Kemp and Peters)
Smoked sheet	345 345	371 (*a*)	372.8
Pale crepe	350 350	374 (*b*)	
GR-S	313 317	341 (*c*)	347
German Buna-S	319 320	?	—

(*a*) Taking rubber hydrocarbon content as 93.0 per cent[14].
(*b*) Taking rubber hydrocarbon content as 93.5 per cent[17].
(*c*) Taking GR-S hydrocarbon as 92.5 per cent[18].

In discussing results obtained with iodine values carried out in the way described, it is convenient to consider a series of results from mixtures containing natural rubber and GR-S in varying proportions as well as vulcanizates containing only one rubber. In the calculation of the actual amounts of rubbers from the iodine value, either the amount of natural rubber or GR-S or the total rubbers, must, of course, be estimated in some independent way. In the results quoted for mixtures, the natural rubber was estimated by the oxidation method. According to U.9, GR-S gives on oxidation, an acid volatile in steam, presumably acetic acid, equivalent to 3 per cent of its weight of natural rubber. The formula given in Table X of Kemp and Peters' paper[16] for percentage GR-S hydrocarbon does not allow for the error in natural rubber hydrocarbon estimation introduced by the presence of GR-S, and it contains, in addition, a printer's error. The results obtained so far do not always justify careful adjustment for the interference, but the correction is included in the equations given.

If R = true percentage natural rubber hydrocarbon.
r = apparent natural rubber hydrocarbon content (*i.e.*, figure obtained in the actual estimation by oxidation, using the 75 per cent factor).
A' = iodine value calculated on unextracted weight of sample. (Kemp and Peters[16] use A = iodine value of acetone-extracted material; but vacuum drying of the extracted material, which their method involved, seemed to lead to difficulties in solution, hence the alternative symbol).

Then, $R = 1.03r - \frac{A'}{112}$.

The corresponding equation for GR-S is:

$$G = 0.298\,A' - 1.11r$$

where G is the percentage of GR-S hydrocarbon in the GR-S.

The actual analytical figures, and those obtained from them by the above equations, are given in Table 5.

TABLE 5

THE USE OF IODINE VALUES IN RUBBER ESTIMATION

Mix number	16	17	18	19	20	21	22	23
A' calculated from	225	190	203	207	216	218	191	182
r	55.9	40.8	31.2	22.5	3.2	—	—	—
G	1.5	11.3	25.8	36.6	60.6	62.8	55.0	52.4
G calculated from mixing formula	0	19.0	28.6	38.5	58.8	57.5	58.9	58.9
R	55.6	40.3	30.3	21.3	1.4	—	—	—
R calculated from mixing formula	56.1	38.1	28.8	19.4	0	—	—	—

It will be seen that, for GR-S, the values obtained are somewhat low on average and the deviation from the true value is higher than is desirable, the mean deviation being 3.92 per cent. This gives an estimated standard deviation of 5.2 and, therefore, one estimation in twenty may be expected to be 10 per cent or more from the true value. There are insufficient values in the table for assessment of the error in estimating natural rubber directly by the iodine value and, at the moment, only a few values are available, the oxidation method having been preferred; these are quoted in Table 6 for comparison with the

TABLE 6

THE USE OF BROMINE VALUES IN RUBBER ESTIMATION

Mix number	26	27	28	29	30
	Rubber hydrocarbon (per cent)				
From bromine value	56.8; 53.3	37.3; 38.8	39.5	38.1; 40.1	48.8; 50.6
From iodine value	60.3	40.2	42.6	46.2	57.8
By oxidation method	55.6	36.7	40.4	43.4	55.5
Calculated from mix formula	56.1	*	*	45.3	*

* Values not calculated, as comparison is not possible in these cases owing to high combined sulfur.

bromine values. They may indicate somewhat smaller errors than those obtained with GR-S.

The successful addition of bromine to the double bond as a means of estimating raw natural rubber is well established if low temperatures are maintained[18]. Schidrowitz[19] commends Bloomfield's procedure to "those condemned to struggle with direct rubber determinations". The possibility of applying this procedure to vulcanized rubber was examined and it was found quite feasible for natural rubber, but not for GR-S and, hence, not for mixtures. The method of solution was the same as that given for iodine values except that cooling, after chloroform has been added, is continued in a freezing mixture and as much chloroform added as is necessary to prevent the *p*-dichlorobenzene from crystallizing. Then, 1–2 cc. of alcohol are added followed by an excess

of a 0.1 *N* solution of bromine in chloroform, the mixture being kept at 0° C for 30 minutes and the excess estimated in the usual way. As with iodine values, blanks are necessary. The excess bromine appears to be liberated from the chloroform layer somewhat slowly, and the titration takes appreciably longer than that in determining an iodine value. Also, some trouble was experienced with emulsification, but a few cc. of ether eliminated this. The results obtained with natural rubber compare favorably with the iodine chloride method, and are given, together with those by the oxidation method, in Table 6. The slight increase in accuracy shown in Table 6 may be more apparent than real, different operators having been employed so that, when allowance is made for the slightly increased trouble, the bromine addition offers no real advantage in estimating vulcanized samples.

With GR-S and mixtures of GR-S with natural rubber, a few preliminary trials (not quoted) gave results far below expectations. Bromination in the cold and at room temperature for different periods of time gave the results summarized in Table 7. Unvulcanized GR-S solution was also brominated

TABLE 7

ESTIMATION OF GR-S BY BROMINE VALUES

Mix no.	Temperature	Time	G from bromine value	G calculated from mix formula
31	0° C	30 min.	31.1; 31.8	58.8
32	0° C	30 min.	69.3	
	Approx. 18° C	15 min.	25.6	87.2
		30 min.	73.1	
		60 min.	78.5	
Unvulcanized GR-S	0° C	30 min.	76.6; 77.7	92.5

cold, and it is obvious that the addition at the double bond is by no means complete under any of the conditions tried. The percentage GR-S is as 75-butadiene-25-styrene hydrocarbon.

This section on the estimation of unsaturation shows that bromine values cannot be used if GR-S is present and, therefore, are limited in vulcanized samples to natural rubber compounds, which are, in general, best estimated by oxidation. Iodine values are of value for GR-S and for mixtures provided chloroprene and its copolymers are absent.

Estimation of butadiene-styrene copolymers by nitration.—This method given fully in U.9, consists essentially in the simultaneous oxidation and nitration of the copolymer, the phenyl groups becoming *p*-nitrobenzoic acid, which is separated by an extraction process and titrated. Natural rubber gives a small amount of extractable acid, so that a correction must be made when estimating mixtures. Also, as mentioned above, a correction must be made for the GR-S present in the estimation of natural rubber by oxidation. Using the same symbols as before, with the addition of s for the apparent styrene content; then, strictly: $R=1.001r-0.1201s$; and $G=4.01s-0.1201r$. It is, however, sufficient to use the formulas $R=r-0.12s$ and $G=4s-0.12r$.

As before, it is convenient to draw examples from analyses of mixtures of GR-S and natural rubber, and the first five compounds of Table 8 are the same as the first five of Table 5, so comparison of the nitration method with the iodine value is possible on a limited scale. The above formulas have been used in making the necessary corrections. Analytical figures on unvulcanized (u) as well as vulcanized (v) material were available.

The results for *G* in Table 8 show that values ranging from 3.6 per cent to 8.8 per cent may be obtained even when no GR-S is present in the mix, and after "correction" of the experimental data. Qualitative analysis is thus advisable, especially if low results have been obtained, so that figures due to the failure of the method in extreme conditions can be discarded.

Unlike the iodine value, styrene estimation gives results somewhat high. Ignoring Mixes Nos. 16, 35, and 36, the mean deviation for GR-S estimation

TABLE 8

THE USE OF STYRENE ESTIMATION IN THE ANALYSIS OF GR-S COMPOUNDS

		16	17	18	19	20	33	34	35	36
R by oxidation method	u.	58.5	40.6	29.6	19.3	4.3	—	—	—	—
	v.*	59.0	39.8	30.1	21.2	1.2	1.6	1.9	74.0	46.2
R calculated from mix formula		56.1	38.1	28.8	19.4	0	0	0	71.0	44.8
G	u.	0	21.6	33.6	45.6	56.8	—	—	—	—
	v.	4.8	24.4	31.2	38.0	62.0	46.4	58.0	8.8	3.6
G calculated from mix formula		0	19.0	28.6	38.5	58.8	48.6	44.5	0	0
Total rubbers from estimation of fillers present	u.	59.5	58.4	54.4	54.3	53.9	—	—	—	—
	v.	54.6	53.9	55.0	57.5	53.2	48.4	49.4	74.6	50.8

* These figures differ from those given in Table 5 because they have been derived by the formula in which correction is made for the GR-S from styrene estimation instead of from iodine value.

is 4.4 per cent and the estimated standard deviation 5.8 per cent. One estimation in twenty will be expected to be 11 per cent or more in error. The figures refer, of course, to the means of duplicate determinations, as is common in analytical practice.

The direct determination of natural rubber is more accurate than the estimation of GR-S from the styrene content, but the sum of these two methods, giving total rubbers present, does not seem to be any more accurate than that obtained by subtracting the total fillers, sulfur, softeners, and other components from 100 per cent. The sum obtained for total rubbers in the corresponding compounds in Table 5 is, apparently, slightly more accurate than that obtained via the total fillers, but there is little in it.

NEW CHEMICAL METHODS OF DETECTION AND ESTIMATION OF OTHER SYNTHETIC RUBBERS

Polyisobutylene.—The method of estimating polyisobutylene in a vulcanizate containing some other rubber and carbon black, given in U.9, has been discarded at the writer's laboratories in favor of simple extraction with petroleum ether after acetone extraction. A vulcanizate containing 65.3 per cent polyisobutylene gave 86.8 per cent by the older method and 62.4 per cent by the new. Full details of the method and a table of comparative results have been published[20].

Polysulfide Materials.—The paper just mentioned gives also a method of differentiating between the two main types of thioplasts. These types are distinguished as disulfides and tetrasulfides, and in the latter the additional two atoms of sulfur are easily removed. Parker has worked out a method

whereby this removable sulfur is estimated in a manner similar to that proposed by Bolotnikov and Gurova[21] for the estimation of free sulfur, and although high accuracy is not obtained, good indication of the actual amount of tetrasulfide, as distinct from disulfide material, can be obtained.

Neoprene-FR.—This can be distinguished from other chloroprene copolymers by the Weber color reaction and from natural rubber by not giving the characteristic color in the trichloroacetic acid test mentioned in connection with detecting natural rubber.

Thiokol-RD.—This is a copolymer of undisclosed composition containing about 4 per cent nitrogen. It can be distinguished from other nitrogen-containing polymers by heating in a distillation flask with aluminum isopropylate in the presence of isopropyl alcohol. A current of air is drawn through the mixture and the liquid coming over is tested with 2,4-dinitrophenylhydrazine hydrochloride (saturated aqueous solution) for acetone; the precipitate (acetone-2,4-dinitrophenylhydrazone) should be recrystallized and a mixed melting point determined.

GENERAL SCHEMES FOR ANALYSIS

Acid resistance as a means of identifying rubbers.—To correct any impression that the identification of synthetic rubber can be made only in a fully equipped chemical laboratory, the first two general schemes to be considered are those requiring a minimum of apparatus. The acid-resistance test[22] enables GR-S acrylonitrile-butadiene copolymers, and natural rubber readily to be distinguished. A small chip of the unknown sample, preferably previously soaked in acetone and dried, is immersed in a mixed acid consisting of equal volumes of concentrated sulfuric and nitric acids. The mixed acid is contained in a test-tube placed in water maintained at 70° C. The time required after adding the sample until the first trace of dispersion or disintegration of the rubber is noted. A table of the ranges within which the reaction times of different rubbers lie is given in the reference quoted. Natural rubber, thioplasts, and chloroprenes cannot be separated by this test, but the latter two are easily distinguishable, the thioplasts by their own odor and the odor of sulfur dioxide on burning and chloroprene by the simple copper-wire test[15]. Provided the sample to be examined is not an awkward mixture of rubbers, identification, at any rate of the type of rubber, can be made with a reasonable degree of certainty.

Swelling ratio in selected solvents.—When a vulcanized rubber sample is allowed to absorb a solvent, the maximum degree of swelling, excluding the continuous increase in swelling due to progressive oxidation, depends on the chemical natures of the polymer and of the solvent, and on the hardness of the compound. Mineral fillers, except in so far as they are responsible for the hardness of the compound, do not affect the maximum. By taking the ratio of the swelling in two solvents, the effect of the hardness of the compound is eliminated, and the use of three solvents enables rubbers to be identified readily; the ratio of swelling in one pair of solvents is plotted against that for another pair and a diagram is obtained which contains areas characteristic of each type of rubber. Identification by this method has been tried extensively with no failure to distinguish types. The method is published[23]. Good results have been obtained without an analytical balance by drawing out glass tubing, mounting the resulting thread in a wooden box and fastening to the thread with sealing wax a small balance pan. A balance of this type will evaluate the

swelling of a very small sample, the swelling maximum of which will be attained in a few hours instead of a few days.

Identification of specific rubbers by their ash.—Polymerization catalysts, emulsifying, precipitating, and creaming agents play a large part in the manufacture of synthetic rubbers, and such reagents, especially those employed in the later stages, are likely to remain in the finished product to a greater or lesser extent. It may be assumed that as long as a particular manufacturing process is employed, the quantitative and qualitative aspects of this contamination will remain reasonably constant. Rubbers of natural origin similarly contain small amounts of mineral elements characteristic of the latex. Quantitative examination of the ash reveals residues of such ingredients, without the difficulty of separation from organic material. The nature of the fillers must be considered also, since these may interfere considerably in specific instances; thus examination for small amounts of phosphorus might be useless in a compound containing whiting. The most useful elements to be examined in the ash have been found to be phosphorus, magnesium, aluminum, and barium. Determination of phosphorus content has been used to determine the natural rubber content of vulcanizates containing it mixed with GR-S or Buna-S[8]. They quote a content of 0.03 to 0.045 per cent phosphorus as indicating natural rubber; 0.01 to 0.025 per cent, a mixture of natural and synthetic; less than 0.005 per cent, synthetic material, the percentages being based on the amount of rubber-like material present. In some unpublished work in 1943 the presence of phosphorus in the correct proportion was used at the Research Association of British Rubber Manufacturers to confirm the natural origin of an alleged synthetic polyisoprene, which, the phosphorus content showed, was made from rubber latex. Working with the method for estimation of phosphorus given in the B.D.H. Book of Organic Reagents[24] and matching the colors developed against standards with the aid of Nessler glasses, the following values, based on reasonable agreement of duplicates, were obtained: smoked sheet, 0.015 per cent; pale crepe, 0.008 per cent; vulcanized latex film, 0.024 per cent; it would appear from the literature, however, that the method cannot be relied upon for distinguishing between smoked sheet and pale crepe rubber. Using phosphorus content as a means of estimating natural rubber, owing to the large multiplication factor involved, does not give good results if reclaim has been employed. Reclaim frequently contains some whiting, and a sample of vulcanized reclaim was found to have 0.056 per cent phosphorus. If the amount of rubber present is known by an independent method, a knowledge of the phosphorus content may serve to indicate the origin of the hydrocarbon, whether from solid rubber or from latex.

The distinguishing of individual rubbers within types is not a matter of casual interest as many means of determining the rubber involve the actual estimation of one group or element in the rubber, and then calculation of the amount of rubber present depending on a prior knowledge of the proportion of that group or element present. Thus, Hycar OR-25 contains 8 per cent, and Hycar OR-15 11 per cent, of nitrogen, and 3.0 per cent of nitrogen in a vulcanizate of this type may represent 37.5 per cent of OR-25 or 27.2 per cent of OR-15.

Table 9 gives the results of qualitative analysis of ash of the more commonly used synthetic products. Useful distinctions which become obvious from the Table are the identification of Chemigum I by the barium content of its ash; a flame test is adequate for this. Hycar-EP, a butadiene-styrene copolymer containing 40 per cent styrene contains aluminum, which has not been found in either GR-S or German Buna-S. Stanco Perbunan, unlike the

TABLE 9

EXAMINATION OF THE ASHES OF RUBBERS

Rubber	% Ash	Phosphorus	Magnesium	Aluminum
Smoked sheet	0.4	††	†	—
Methyl rubber	0.2	—	—	—
Buna-85	0.7	—	†	—
Buna-115	0.8	—	—	—
Buna-S	0.2	†	—	—
GR-S	0.7*	—	†	—
Hycar-EP	0.9	—	—	††
German Perbunan	0.1	—	††	—
Stanco Perbunan	0.2	—	—	—
Chemigum I‡	5.2	—	††	††
Hycar OR-15	0.9	—	††	†
Hycar OR-25	?	—	†	†
Thiokol-RD	1.5	—	††	—
Neoprene-CG	1.1	—	—	—
Neoprene-E	0.5	—	—	—
Neoprene-GN	0.3	—	—	—
Neoprene-FR	2.0	††	††	—
Neoprene-KNR	2.0	††	††	—
Neoprene-I	0.4	††	—	—
Neoprene-Z	0.7	††	—	††
Thiokol-AZ	0.4	††	—	†
Thiokol-FA	2.5	—	†	††
Thiokol-F	0.6	—	††	††
Thiokol-N	?	—	††	†
Polyisobutylene	0.1	—	—	—

* More recent samples give 1.4 per cent ash, and alum-coagulated polymer may be expected to contain aluminum.
†† Element present.
† Trace only of element present.
‡ Chemigum-I contains appreciable quantities of barium.

other acrylonitrile-containing polymers listed, does not seem to contain any of these elements. There are also some distinctions between the various Neoprenes which might be useful should need arise.

The remainder of the ash is usually iron, sulfate, sodium, and potassium possessing no diagnostic value.

Ultraviolet fluorescence has been tried in a similar way, but with disappointing results. The inspection was visual, using a mercury vapor lamp with a Wood's glass filter. No spectroscope was available for identification of any "tracer" elements. Most raw synthetics showed marked fluorescence varying with a few exceptions from pale lavenders and blues to dark mauves. The vulcanizates, which all contained carbon black, showed either dim fluorescence of the same shade as the raw material, or else none. The ashes of the raw synthetics were without fluorescence except Hycar OR-15, which showed a mauve fluorescence. Confirmation on other batches of OR-15 is desirable.

Use of infrared spectroscopy.—That portion of electromagnetic radiation known as the infrared may be said to have wave lengths between 10^{-4} cm. up to 1 cm., although only a fraction of this range, approximately up to 2.5×10^{-3} cm. is normally used in spectroscopy. It is in the infrared that many of the characteristic frequencies of organic molecules lie when they are bending, twisting, rotating, vibrating, or deforming in any way. This vibration, or deformation, must, in a nonpolar molecule, be accompanied by a change in dipole moment if energy is to be absorbed or radiated. Thus, a molecule not possessing a permanent dipole does not absorb energy on rotation about an

axis of symmetry, but may do so if some other type of oscillation results in a change of dipole moment. The quantum theory postulates discrete values of angular moments; hence a spectrum containing definite frequencies is obtained. The energy required for the various movements mentioned is determined, depending on the type, by the moment of inertia, atomic mass, force constants of the bonds connecting the atoms of the molecule together, and dipole moment, if any. In practice, the source of radiation is a Nernst glower, and absorption is measured by comparison of intensity of the radiation with and without the specimen. Photography is of little use in measuring intensity (the best plates record only from the visible spectrum up to 1.3×10^{-4} cm.) and thermoelectric devices are used with galvanometer relays or, more recently, d.c. amplifiers. Percentage absorption is given by $\left(1 - \frac{I}{I_0}\right) \times 100$ where I/I_0 is the ratio actually measured on the spectrograph tracing, I being the intensity after absorption and I_0 that without absorption. Comparisons made with standard samples under fixed conditions are normally sufficient for analytical purposes, but if correction is to be made for thickness of sample, Beer's law can be applied. This gives $\frac{I}{I_0} = e^{-kcx}$, where k is the extinction coefficient of the substance at the given frequency; c is its concentration, and x is the length of path used. Log I/I_0 is called the optical density, and where chemical interaction does not occur, the optical density of a mixture can be assumed to be the sum of those of its components. It should be noted that, in analyzing mixtures, the complete spectral map need not be ascertained, only quite narrow regions being used where frequencies characteristic of the components to be estimated are found conveniently free from interference due to irrelevant materials, such as the solvent if a solvent is employed. A good introduction to the origin of infrared absorption spectra is given by Thomson[25]. There are several papers dealing with its use in analysis, and Barnes and his collaborators[26] and Thompson and Sutherland[27] have been drawn upon in the following.

Turning to applications of infra-red spectroscopy to synthetic rubbers, raw materials can either be dissolved in a solvent, the spectrum of which does not interfere, or sections can be cut, as the material is reasonably transparent. Accurate quantitative work, however, has yet to be achieved. With vulcanized rubbers containing carbon black, dissolution in a high boiling oxidizing solvent and removal of carbon black seems the only way. This is the method adopted by Barnes and his collaborators.

Considering the spectra of rubbers and their allied compounds there is, already, a fair amount of data on which to base a preliminary study of spectra. Unfortunately, the data are not reported very consistently in the literature, and the uninitiated are warned that whereas the American articles quoted give spectral maps of absorption spectra in which percentage transmission is plotted against wave numbers, *i.e.*, reciprocal wave lengths, which they call frequency, British publications plot percentage absorption, so that the peaks in one series of diagrams are the troughs in the other and *vice versa*. A similar but minor matter is that in the recent symposium on infrared spectroscopy already mentioned, some papers quote wave lengths in μ, and others wave numbers. Some convention seems desirable. Reference has already been made to the fact that as an analytical technique applied to rubbers, accuracy has yet to be achieved. Barnes and his collaborators mention 5 to 10 per cent, but do not quote results obtained on mixes of known composition. Instead, they give analysis of

enemy samples, and the figures quoted are rounded off to the nearest five or ten. The criteria these workers used are given in Table 10.

TABLE 10

CHARACTERISTIC ABSORPTION PEAKS IN INFRARED SPECTRA OF RUBBERS

Rubber	Position of peak in wave numbers	Group of which this is characteristic
Natural rubber	1380 cm.$^{-1}$	$-CH_3$
	835	$R_2C{=}CHR$ (?)
Buna-S	1500	Phenyl group (1st harmonic)
	970	probably due to 1,4-addition
	917	of butadiene

The phenyl group can be observed[28] also at 760 cm.$^{-1}$ and any 1,2-addition of butadiene shows characteristically at 909 and 990 cm.$^{-1}$. Calibration was done against mixtures of known composition. It is probably more satisfactory to obviate the difficulties in preparing specimens of known uniform thickness by using an internal calibration, such as the extinction coefficient of one of the groups present. This involves knowing its absolute value and demands that this value should be independent of the group to which it is attached[29].

CONCLUSION

There is considerable overlap between the various methods reviewed above, some of which are completely self-contained, whereas others have to be grouped together to provide a complete analytical scheme. There are, consequently, several ways of building up a comprehensive system, and which way is preferred in practice depends on the amount of information already in the possession of the analyst, and his purpose in carrying out the analysis. In the case of an unknown vulcanized sample requiring full investigation, the following order of procedure will be found helpful.

(1) Sufficient of the rubber for the tests required is acetone-extracted and dried.

(2) Preparations for determining swelling ratios should be made. Unless the modified micro-method is used this result will not be available for a week. However, it is definitely worth starting as the preparations take only the time required for weighing and although the rest of the analysis will be completed, confirmation of such work arriving after a few days will be valuable as in independant check and an insurance against error or accident.

(3) The systematic scheme for qualitative analysis given in U.9 should be used, starting with the sodium fusion for elements. Even if elements characteristic of certain types are present, it must be assumed that hydrocarbon polymer is present also and that part of the scheme given for cases where characteristic elements are absent should be used. It may, however, be abbreviated by limiting it to the use of color tests for natural rubber and GR-S, although there is danger of missing the presence of alkali reclaimed natural rubber if this is done.

(4) From the qualitative composition such rubbers, as are indicated present, are determined quantitatively.

(5) It is useful to make certain that the results obtained are in agreement with any physical properties that can readily be noted, *e.g.*, freeze resistance and specific gravity.

ACKNOWLEDGMENTS

The author's thanks are due to (Miss) A. D. Richards, (Miss) W. M. Phillips, and (Miss) E. Boroff for performing many of the analyses quoted, to the controller of Chemical Research and Development, Ministry of Supply, for permission to refer to The Services Rubber Investigations, Users' Memorandum U.9, and to the Research Association of British Rubber Manufacturers for allowing publication of this paper.

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FACTORS AFFECTING RESULTS OBTAINED WITH THE MOONEY VISCOMETER *

ROLLA H. TAYLOR

NATIONAL BUREAU OF STANDARDS, WASHINGTON, D.C.

I. INTRODUCTION

Studies of the results obtained with Mooney viscometers in measurements of viscosity of synthetic rubbers indicate the need for better and more definite instruction of operators of such viscometers. Recent reports of tests made on standard bales of raw GR-S at eighteen different laboratories show that readings for individual tests vary over a range of approximately 12 units and that averages obtained by the different laboratories vary over a range of 4.5 units. If suitable precautions are taken, individual values from different laboratories need not vary by more than 3 units, and the average values from the different laboratories should vary by less than 1 unit.

To attain this degree of agreement in different laboratories, it is essential that precautions be taken in caring for and adjusting Mooney viscometers with respect to the following five items: (1) the machine must be clean; particularly there must be no rubber in the bearings on the vertical shaft; (2) the machine must be mechanically calibrated to rigid specifications; (3) the dies, die holders, and rotors must be of specified dimensions; (4) the die closures must be carefully adjusted to rigid specifications, and (5) the test-pieces used in the machine must be carefully prepared and selected for accuracy of dimensions and freedom from air. A well constructed machine with all operating parts machined to proper tolerance is of course implied.

This paper describes the precautions that must be taken and the methods of adjustment that must be followed if uniformity in the values of Mooney viscosity are to be obtained on the same samples with different viscometers and in different laboratories. The variations that may result if the outlined procedures are not closely followed are discussed.

II. EFFECTS OF INADEQUATE OR INFREQUENT CLEANING OF THE MOONEY VISCOMETER

It is of the utmost importance that certain parts of the Mooney viscometer be kept absolutely free from rubber at all times. Results obtained from tests made on machines that have rubber in the bearings can never be depended upon, and tests made on machines operated with the serrations on the dies and rotors clogged with rubber are very apt to give erroneous results.

1. *Effects of Rubber Around the Top of the Vertical Shaft.*—In AA and earlier model viscometers, by far the most important cleaning operation, and the one which has been the hardest to bring to the realization of Mooney operators, is the removal of rubber from around the top of the vertical shaft (see Figure 1 for location of parts). The lower die should be removed, and any rubber that

* Reprinted from *Circular of the National Bureau of Standards C451*, November 8, 1945.

has leaked past the rotor stem should be cleaned out so that it will not be forced into or work itself into the top bearing. No definite rule can be established for the regularity with which this cleaning operation should be performed because of the variables involved. The amount of rubber that will leak past the rotor stem depends on the clearance between the rotor stem and the lower die and on the plasticity of the rubber being tested. The amount of rubber that can safely be permitted to leak into the chamber at the top of the vertical shaft before cleaning depends chiefly on the clearance between the top of the vertical shaft and the bottom of the lower die. Frequently, maintenance personnel in replacing the bronze bearing in the upper part of the housing have not realized the importance of this clearance and have left the bearing too long, so that the

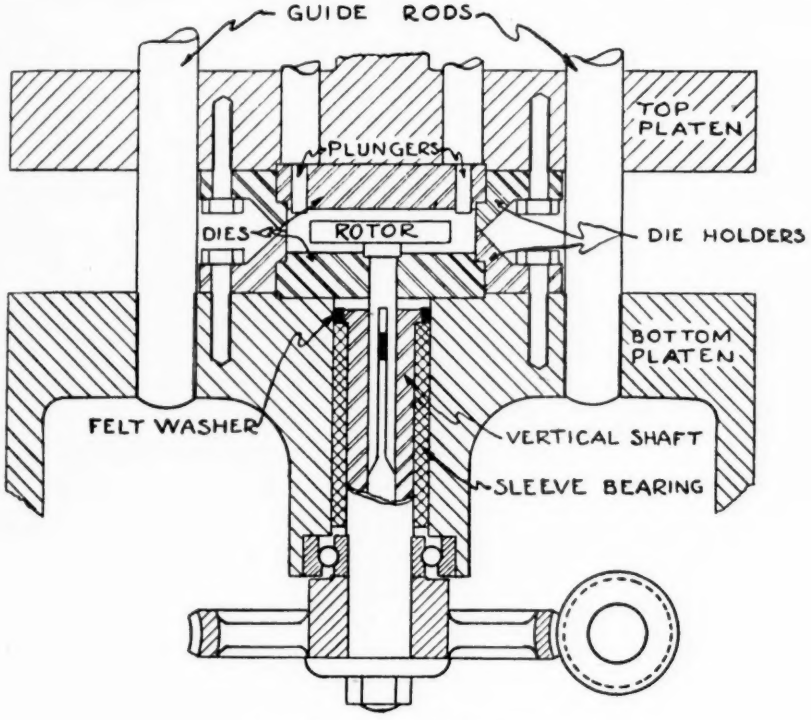

FIG. 1.—Section of Mooney viscometer.

clearance was reduced to less than $\frac{1}{16}$ inch. In fact, one case was encountered in which it was so small that not more than one test could be made without obtaining erroneous results. The design of this instrument calls for a clearance of $\frac{1}{8}$ inch. It is recommended that it be not less than $\frac{3}{32}$ inch on any machine. It should be borne in mind also that it is desirable to have the top of the vertical shaft as high as practicable in order to give the necessary support to the rotor.

A well-oiled felt washer at the top of the vertical shaft has been found quite helpful in preventing the rubber from working its way into the bearings. Some laboratories have not found these washers to be of any help, simply because their cleaning periods were so infrequent that rubber was forced into the felt washer, rendering it useless and in time destroying it. Proper cleaning and

oiling permitted the use of one felt washer at the National Bureau of Standards for a period of more than 6 months without the necessity of removing it or the vertical shaft.

Normally a small amount of rubber leaks past the rotor stem each time that a test is made. Assuming sufficient clearance between the top of the vertical shaft and the lower die, this rubber lodges on the top of the shaft without affecting the viscometer reading. As rubber is forced into the space between the die and the shaft, it is rolled between the two without materially affecting the results. Then, as more rubber is forced past the rotor stem it completely fills the space between the die and the shaft and finally is forced down into the bearing. Should this happen, the only way in which the machine can be properly cleaned is by removing the vertical shaft and cleaning thoroughly both the shaft and the bearing. If this is not done, the results at best are bound to be unreliable.

Mechanical calibration designed to compensate for the increased friction due to the rubber in the bearing should never be tolerated. In most cases where this is done, high values of viscosity are obtained, because the increased pressure due to additional leakage of rubber during a test increases the friction still more. The errors resulting from this condition have been found to be as much as 6 units.

When the felt washer is not used at the top of the vertical shaft, any rubber that leaks past the lower die is likely to find its way into the bearing, and it is never certain just how much the results are being affected by this condition.

The only way in which to be sure that the results are not affected is to have a felt washer at the top of the shaft, keep it well oiled, and above all, remove the lower die and clean out the rubber before it has been forced into the felt. Approximately 10 minutes is required to remove the lower die, clean out the rubber, oil the felt, and replace the die. On the other hand, 2 hours or more is required to remove the vertical shaft and perform the necessary cleaning operation after rubber has been forced into the bearing, and it is never certain just when the excess rubber begins to affect the readings.

The design of the new NBS model Mooney viscometer alleviates some of the difficulties of cleaning required in the earlier designs by increasing the size of the cavity at the top of the vertical shaft, by using a better bearing shield at the top of the shaft, and by using a sealing washer in the lower die. This does not mean that rubber leakage through the lower die has been eliminated, nor does it mean that cleaning is no longer necessary. The frequency of cleaning, however, has definitely been decreased. Oil at the top of the shaft is not recommended for the NBS models; otherwise the above discussion applies to these models as well as to others.

2. *Effect of Rubber in the Serrations of the Dies and Rotors.*—It is highly important that any rubber which sticks to the dies and rotors and fills the serrations of these parts should be removed before proceeding with the next test. The greatest errors are experienced when a test on rubber of low viscosity is followed by one of higher viscosity. The error is caused by shearing of the rubber that remains in the dies and on the rotor near the surface of these parts rather than shearing of the sample itself. Insufficient data are available to show the extent of such error, but low readings have been observed in cases where the operator has failed to clean the rubber from the serrations on the rotor and in the die cavity.

3. *Effect of Rubber Around the Plungers.*—The frequency with which the plungers require cleaning depends on the clearance between the plungers and plunger holes in the top die, the kind of samples being tested, and the precau-

tions taken to keep the plungers from becoming clogged. Rapidly working the plungers up and down several times after every few tests tends to keep them free and in good working order. In fact, if this procedure is performed regularly, the viscometer can be operated continuously for weeks without having to remove the plungers for cleaning.

Inoperative plungers cause the viscometer reading to be low. Where there is no plunger action at all, the error introduced may be as much as 3 units.

Oil should never be applied to the plungers because it causes the rubber that leaks past the upper die to become sticky and more difficult to remove from the plunger parts.

III. MECHANICAL CALIBRATION

Mechanical calibration of Mooney viscometers, although somewhat tedious, is a straightforward procedure that should not give undue trouble. It is, nevertheless, a very important step that must be taken to insure correct readings of viscosity.

There has been considerable discussion as to whether it is sufficient to calibrate viscometers at the normally specified reading of 100 or whether they should be calibrated at or near the reading that is obtained from the rubber tested. Actually, it makes no difference as long as the **U**-spring is not stressed beyond its elastic limit, since the calibration curve for the **U**-spring is then a straight line. A few cases have been found where an error was introduced as a result of permanent set taken by the **U**-spring when rubbers having a high viscosity were tested. This means that in these particular cases the spring was stressed beyond its elastic limit. Consequently, the results would not be dependable, regardless of the point at which the calibration was made. Any **U**-spring designed for use on the viscometers that does not give a straight-line relation between load and deflection should not be used.

IV. EFFECTS OF DIMENSIONS OF DIES, DIE HOLDERS, AND ROTORS

The dimensions of the die cavity and the dimensions of the rotor head are very important from the standpoint of attaining uniform results with different Mooney viscometers.

Mooney[1] gave the following equation for the Mooney viscometer reading in terms of constants for a particular instrument and the average viscosity of the sample being tested.

$$G = \frac{\eta_m}{181.44gP}\left(\frac{4\pi\Omega}{a}\int_0^R r^3 dr + \frac{2\pi h R^3 \Omega}{b}\right)$$

which may be reduced to

$$G = \frac{2\pi\eta_m \Omega R^3}{181.44gP}\left(\frac{R}{2a} + \frac{h}{b}\right) \tag{1}$$

where all the terms are expressed in cgs units and

G = Gauge reading
η_m = Average viscosity
Ω = Angular velocity of rotor in radians per second
g = Gravitational acceleration
P = Pitch radius of worm gear
R = Radius of rotor
a = Vertical clearance between rotor and stator above or below the rotor
h = Thickness of rotor
b = Effective radial clearance between rotor and stator.

1. *Effect of Dimensions of Rotors.*—For the purpose of calculating the effect of sizes of rotor on the viscometer reading, we may assume the average viscosity (η_m) to be a constant that will give a gauge reading of 50 for rotors and dies of specified dimensions. Then, since g, P, and Ω are constant, we may write:

$$G = KD^3\left(\frac{D}{4a} + \frac{h}{b}\right) \tag{2}$$

where K is a constant, D is the diameter of the rotor, and D, a, h, and b are all measured in inches. Now, since the inside diameter of the die holder is to be 2.000 inches, and the total depth of the chamber is to be 0.418 inch, we may write:

$$a = \frac{0.418 - h}{2} \tag{3}$$

and by Mooney's reasoning,

$$b = \frac{1}{2}\left(\frac{3}{2}a + \frac{2.000 - D}{2}\right) \tag{4}$$

to a close approximation.

If we now assume values for D and h and calculate G, the curves shown in Figure 2 are obtained. Thus we see that the viscometer reading for the sizes of rotors considered vary at the rate of approximately 0.25 unit per 0.001 inch change in the diameter of the rotor.

To check the theory presented above, tests on Vistanex were made with four available rotors and the results compared with the calculated value for each rotor. These comparisons are shown in Table 1.

TABLE 1

EFFECT OF ROTOR DIMENSIONS ON VISCOMETER READING

	Rotor number			
	1	2	3	4
Rotor dimensions, in inches:				
Diameter (D)	1.502	1.502	1.507	1.510
Burr diameter*			1.516	1.518
Thickness (h)	0.220	0.221	0.219	0.226
Viscometer reading:				
Sample 1—				
Observed value	49.5	51	52	53
Calculated value based on:				
(1) Diameter		49.8	50.0	52.2
(2) Burr diameter			51.4	53.5
Sample 2—				
Observed value	55.5	55.5	57	58.5
Calculated value based on:				
(1) Diameter		55.8	56.1	58.5
(2) Burr diameter			57.6	60.0

* Burrs were formed at the corners of the rotor during the chromium-plating operation. The burr diameter is taken as the maximum diameter of the rotor including the burrs.

For purposes of calculation, 49.5 and 55.5, the values obtained with rotor No. 1 were assumed to be the correct gauge readings for rotor No. 1, and were used in calculating the constant K in Equation 2 and the expected results for rotors Nos. 2, 3, and 4. It should be noted that the calculated gauge reading is related to the effective values of D and h, and that these may or may not be

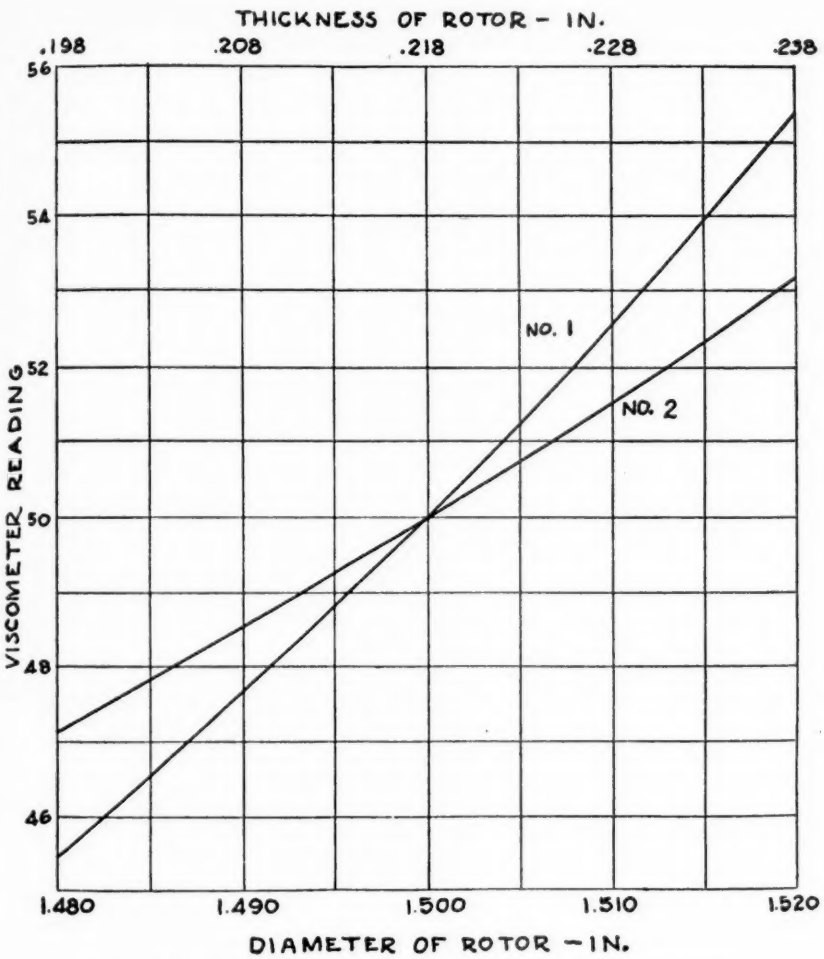

FIG. 2.—Calculated effect of thickness and diameter of rotor on viscometer reading.

Curve 1—thickness.
Curve 2—diameter.

the same as the measured values. This is particularly true where the rotor has burred edges, as was the case with rotors Nos. 3 and 4.

2. *Effect of Dimensions of Die Cavities.*—Changes in the depth and inside diameter of the die holders affect the gauge reading insofar as they affect changes in the values of a and b, respectively. If the rotor head is assumed to be 1.500 inches in diameter and 0.218 inch thick and the dimensions of the die cavity are permitted to vary, Equations 3 and 4 become:

$$a = \frac{T - 0.218}{2} \tag{5}$$

and

$$b = \frac{1}{2}\left(\frac{3}{2}a + \frac{d - 1.500}{2}\right) \tag{6}$$

where T is the total depth of the die cavity and d is the diameter of the cavity. From an analysis of Equations 2, 3, 4, 5, and 6, it can be shown that the change in the viscometer reading with an increase in T is essentially equal to the change reading resulting from a decrease in h equal to the increase in T, and *vice versa*. The change in reading is approximately 0.25 unit per 0.001 inch change in the total depth of the die cavity, whereas the change in reading resulting from a change in the diameter d is only about 0.15 unit per 0.010 inch change in d. It will be noted from Equations 2 and 6 that the effect of changing the inside diameter (d) of the die cavity is much less than the effect of changing the diameter (D) of the rotor.

As the variations in the dimensions of the rotors studied are not so great as those encountered in different plants, the variations in viscometer readings shown in Table 1 are not so great as those found in actual practice. However, they do indicate the conformance of observed data to theory, and the curves shown in Figure 2 indicate the importance of using only rotors, dies, and die holders that conform to the specified dimensions. The dimensions and tolerances usually recommended are given below as a matter of interest:

Rotor:			
Head diameter	1.500	+0.001	−0.001 in.
Head thickness	0.218	+0.001	−0.001 in.
Dies:			
Total thickness	0.509	+0.000	−0.001 in.
Thickness from bottom to shoulder	0.406	+0.000	−0.001 in.
Die holders:			
Thickness from shoulder to closing face	0.312	+0.000	−0.001 in.
Inside diameter	2.000	+0.010	−0.000 in.

3. *Effect of Position of Rotor Head.*—The Mooney viscometer readings are affected not only by the dimensions of the die cavity and the rotor but also to some extent by the position of the rotor in the die cavity. It is intended that the rotor head shall operate in the exact center of the die cavity. In the A

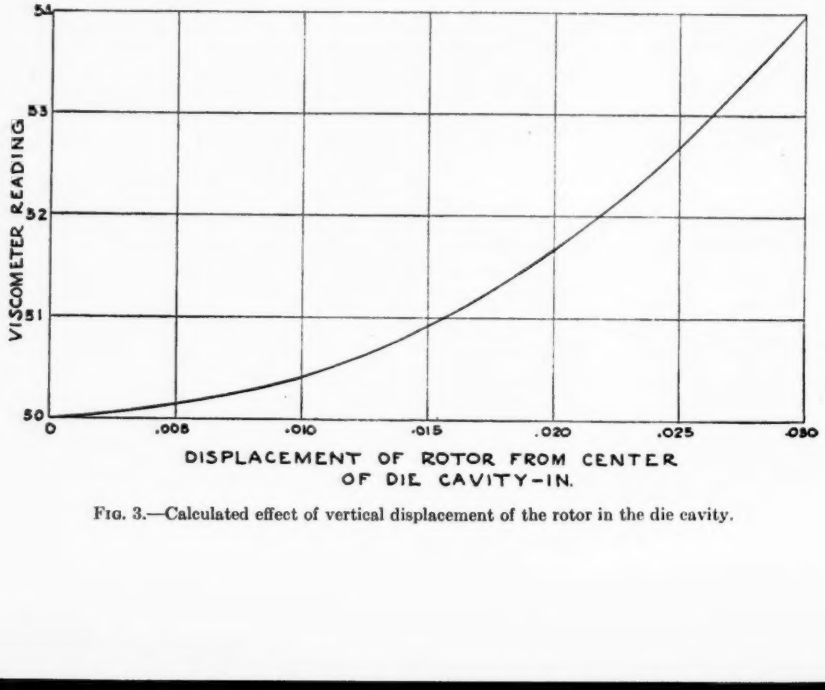

FIG. 3.—Calculated effect of vertical displacement of the rotor in the die cavity.

and AA model viscometers, however, it is impractical if not impossible to maintain the rotor in this position because of the rapid wear which takes place between the shoulder on the rotor stem and the lower die. This difficulty is not present in the NBS model. As long as the dimensions of the various parts are such that the rotor is properly positioned to begin with, one can be reasonably sure that the correct position will be maintained.

The rotor head can be off the central position by 0.01 inch without materially affecting the results. But no more than 0.01 inch should be permitted. Where the rotor is off center by 0.03 or 0.04 inch, the viscometer readings may be increased by 2 or 3 units. A very practical way to check the position of the rotor is to compare the thickness of the cross-sections of the portions of the test-piece from above and below the rotor.

The curve in Figure 3 shows the effect of displacing the rotor head from the central position of the die cavity. This curve was calculated from Equations 2, 3, and 4, and it correlates reasonably well with experience.

V. ADJUSTMENTS

Correct adjustment of the die closure is without doubt the most difficult to attain of the five items discussed in this paper. It has not been found possible to set forth a method of adjustment that is free from the personal factor, nor has it been possible to convince all operators of the importance of careful adjustment. Several different methods of adjustment have been tried, none of which are entirely satisfactory. Considerable progress has nevertheless been made.

Correct adjustment of the die closure is considered to be a condition such that when the mating surfaces of the die holders are forced together there will be a uniform pressure at all points between the two surfaces. The pressures are not great enough to cause undue strain in any of the parts, and yet the pressures are great enough to eliminate practically all of the leakage from the die cavity between the closing surfaces. The following method is suggested for making this adjustment.

1. *Adjustment of Plungers and Dies.*—Replace the upper die and plungers, being careful to aline the die with the plungers. Place the die holder (TD in Figure 4) over the die and hold it firmly in place while applying the four cap screws that hold the die holder and die in place, being careful to tighten opposite screws evenly. Do not tighten the cap screws too much. Just bring them up snug.

If the plungers do not operate freely after the die and the plungers have been tightened in place, loosen the studs in the die holder and in the plunger clamp and shift them into a position that permits the plungers to operate freely.

Check the operation of the plungers by rapidly raising and releasing the plungers several times. (Recheck the operation of the plungers frequently throughout the day, as they tend to pick up rubber and become inoperative very quickly, especially when compounded samples are tested. Clean them whenever necessary, as indicated in Section II, 3.)

Oil the felt washer around the top of the vertical shaft in models A and AA, as outlined in Section II, 1. Replace the lower die. Start the motor, insert the rotor and align the die by shifting it to the position at which the magnitude of the periodic fluctuations of two per minute is a minimum. Place the die holder on the die and tighten the four cap screws as was done on the upper die, being sure that the fluctuations are not increased by this operation.

Make a pattern of the die closure (C) by placing a piece of thin (not thicker than 0.0015 inch) soft tissue paper between the dies and closing the machine. Adjust the four cap screws in the die holders until a continuous pattern of uniform intensity is obtained. Do this by tightening the cap screws adjacent to the part of the die holder which produced a pattern of high intensity, and

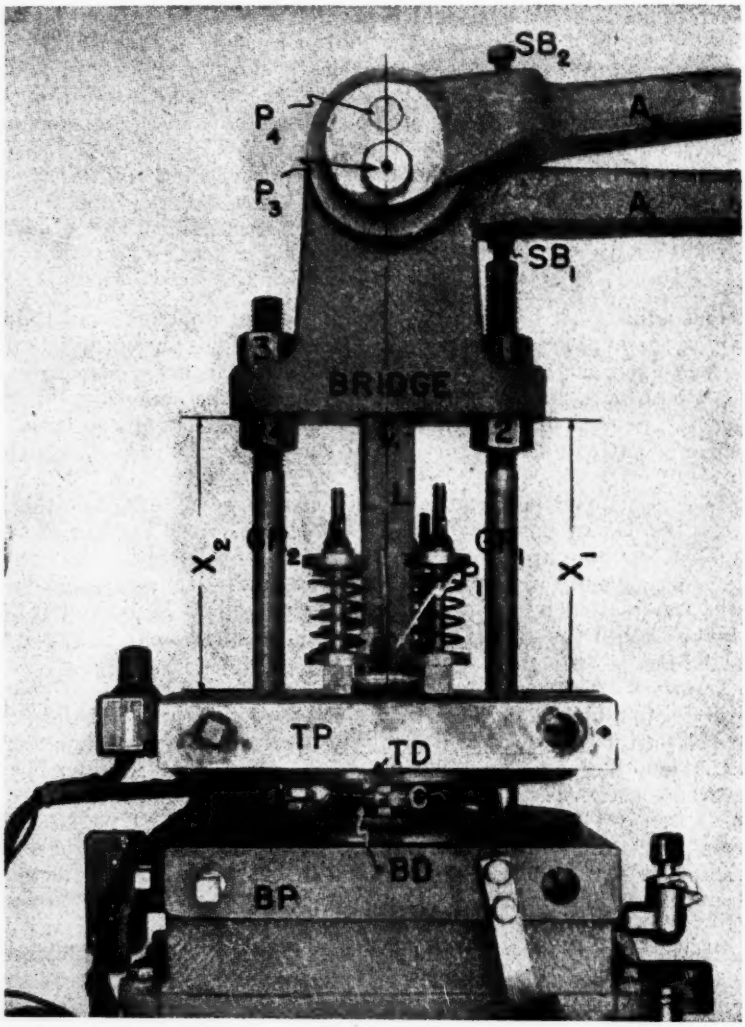

FIG. 4.—Mooney viscometer.

loosening those adjacent to the part which produced a pattern of low intensity. If a perfect pattern cannot be obtained in this manner, remove the four cap screws from the lower die holder (BD), turn the die holder one-quarter turn and proceed as before. If, after trying each position of the die holder, a pattern of uniform intensity has not been obtained, replace the die holder with a new

one. To aid in relocating the correct position of the die holders when replacing them after cleaning, place a reference mark on them.

2. *Adjustment of Platens.*—Make the following adjustments, with the platens at the temperature of the test:

(1) Adjust the position of the bridge so that the distances X_1 and X_2 in Figure 4 are equal when the dies are closed, by adjusting the guide rod nuts 1, 2, 3, and 4 on guide rods GR_1 and GR_2.

(2) Adjust the position of the link (L), which connects the top platen (TP) with the lower lever arm (A_1) so that the link is on dead center when the dies are closed; *i.e.*, so that the four pins P_1, P_2 (not shown—connects L with A_1), P_3, and P_4 all lie on the same center line. Do this by adjusting the stop bolts

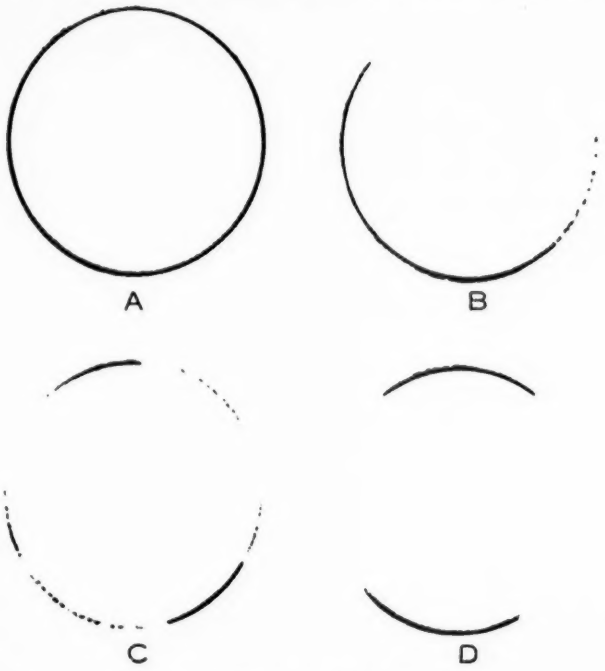

FIG. 5.—Typical patterns of die closures.

A, Good die pattern; B, poor because of cocked die holder; C, poor because of badly worn die holder; D, poor because of nonuniform tightening of die holder or inequality in thickness around die from bottom to shoulder.

SB_1 and SB_2. Turn the stop bolt (SB_1) out of the guide rod (GR_1) to swing the link forward at the top. Turn the stop bolt (SB_2) out of the lever arm (A_2) to swing the pin P_3 toward the back and the pin P_4 toward the front of the machine.

(3) Mark the position of two adjacent corners of the hexagon nuts 1 and 3 on the bridge with a pencil for reference. In all subsequent adjustments involving the nuts on guide rods GR_1 and GR_2, loosen nuts 2 and 4, then make the necessary adjustments by turning nuts 1 and 3. Be careful to turn both nuts exactly the same amount with reference to the pencil marks placed on the bridge, and then tighten nuts 2 and 4. Place four springs between the platens, one at each corner. The plunger springs originally supplied on the first AA

models are suitable. If these are not available, similar springs may be made by winding $\frac{1}{8}$-inch spring wire on a 0.665-inch-diameter rod. The finished spring should be about $2\frac{5}{8}$ inches long and have a $\frac{3}{8}$-inch pitch. Adjust the height of the bridge so that, after the top platen has been raised and lowered with the springs in place, a 0.002-inch feeler gauge can just be passed between the closing surfaces of the die holders at some one point but so that a 0.004-inch feeler gauge cannot be passed between the die holders at any point. Loosen nuts 2 and 4. Turn nuts 1 and 3 down exactly one-twelfth turn (one-half of one face of the nuts) and tighten nuts 2 and 4 to give the correct die pressure.

(4) Recheck items (1) and (2) above. Also check the die pattern as described in Section V, 1. Make further adjustments if necessary. If it is found necessary, on rechecking, to adjust for items (1) and (2), make readjustments as specified in Item (3).

Adjustment of the die closure as outlined above produces a total deformation of parts of from 0.004 to 0.006 inch, which is distributed throughout the dies, die holders, platens, guide rods, connecting link, bridge, and lever system. The amount of this deformation is determined by the adjustments and the fact that the guide rods have 11 threads per inch. Thus the bridge is raised or lowered 0.091 inch per turn of nuts 1 and 3. As all play in pins P_1, P_2, P_3, and P_4 is assumed to be taken up by the action of the springs between the platens, and as the bridge and upper platen assembly is moved down approximately 0.008 inch by turning nuts 1 and 3 down one-twelfth turn, the difference between 0.008 inch and the clearance between the mating surfaces (0.002 to 0.004 inch) is from 0.004 to 0.006 inch, and this must be accounted for by actual deformation of parts.

It is difficult to show a direct correlation between viscometer readings and the amount of deformation that would take place by a particular adjustment. It is well known, however, that as the die closure becomes looser the reading decreases, and as it becomes tighter the reading increases. It is not definitely known whether the increased reading in the latter case is due to increased pressure on the test-piece or increased friction in the machine due to deformation of parts. Probably the reading is influenced by both. As the closing pressures are decreased, the reading is influenced principally by the amount of the leakage that takes place. Actual cases have been observed where maladjustment of the die closures resulted in errors of plus or minus 5 units, depending on whether the closures were too tight or too loose. It should be noted also that, even if the pressure on the die closure is too high, the reading may be low in cases where a badly worn die holder or poorly adjusted die holders permit undue leakage.

VI. PREPARATION OF TEST PIECES

The viscosity value obtained for a given material depends not only on the condition of the viscometer but on the preparation of the test-piece as well. The test-pieces should be not less than $\frac{3}{8}$ inch thick, so that one test-piece below the rotor and one above the rotor completely fills the die cavity, with sufficient overflow to force the rubber into the corners of the die cavity and to force out as much air as possible. The test-pieces should also be as free from air as it is practical to make them, and they should be free from pockets, which may trap air against the rotor or die surfaces. Furthermore, the test-piece placed below the rotor should have a hole punched through its center and be slipped over the rotor stem. Test-pieces should never be cut and slipped around the rotor stem, since this method frequently traps air in the die cavity.

The statement has been made that air works out of the test-piece and escapes through the plunger holes during operation of the machine. The writer has observed, however, that very little, if any, air escapes from the die cavity, once the test-piece is in the machine and the dies are closed. Normally part of the trapped air is absorbed by the specimen and the remainder collects in small pockets near the center of shear. This may be readily verified by observing the cross-section of test-pieces that contain considerable air at the time they are placed in the machine. Air in the test-pieces may lower the whole viscosity time curve by 1 or 2 units, and usually causes a much greater drop during the first two minutes of operation.

With the exception of GR-I, and possibly GR-M, suitable test-pieces seldom can be prepared directly from bales of rubber obtained commercially. Some milling is required to eliminate at least part of the air and to knit the sample together. It is important, however, that rigid specification for milling be followed to get reproducible results between samples of the same material. In general, the Mooney viscosity is quite sensitive to milling, particularly during the first part of the milling operation. Figure 6 shows the effect of milling on the Mooney viscosity for natural rubber, GR-M, GR-S, and GR-I.

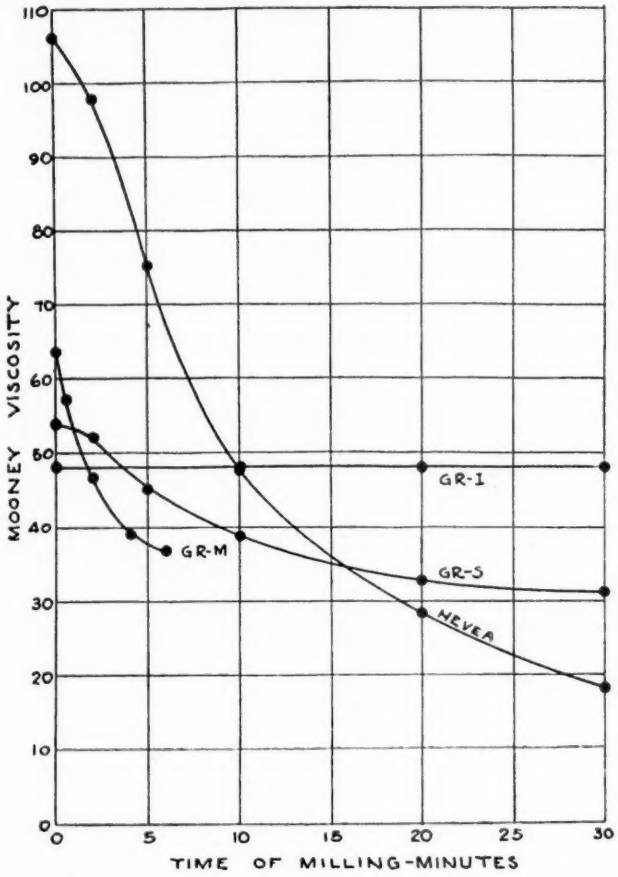

FIG. 6.—Effect of time of milling on viscosity of different rubbers.

In testing compounded stocks, not only the extent of milling and amount and kinds of compounding ingredients affect the viscosity but also the mill temperature. Figure 7 shows the relationship between Mooney viscosity and mill-roll temperature for X-179 GR-S compounded in accordance with the specification for GR-S issued by the Rubber Reserve Company.

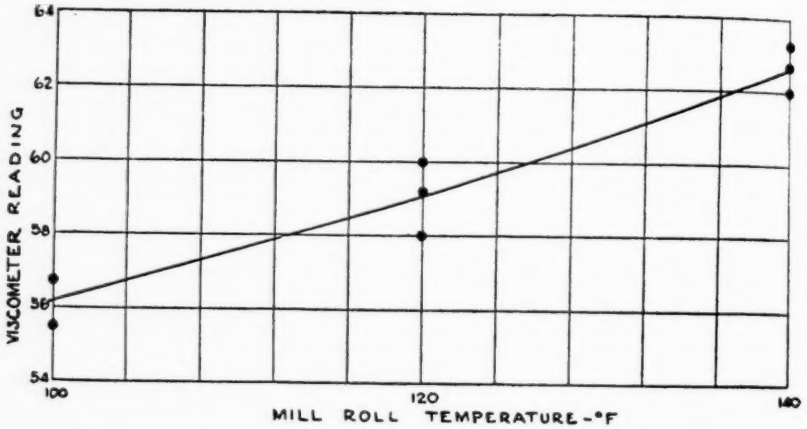

FIG. 7.—Effect of temperature of mill rolls during compounding on viscosity of GR-S.

SUMMARY

Experience with the operation of the Mooney viscometer in 18 laboratories indicates the need for better reproducibility of results. A study of the available data from these laboratories along with numerous experiments made at the National Bureau of Standards have shown the factors that must be considered in improving the reproducibility. If uniformity in the values of Mooney viscosity on the same sample with different viscometers and in different laboratories is to be obtained, the methods of adjustment that must be followed and the precautions that must be taken are cleaning, mechanical calibration, dimensions of dies, die holders, and rotors, die closures, and preparation of test-pieces. Each of these items and the errors which may result from maladjustments and lack of precautions in the use of this instrument are discussed.

REFERENCE

[1]Mooney, *Ind. Eng. Chem. Anal. Ed.* **6**, 147 (1934).

USING THE MOONEY VISCOMETER *

J. M. BUIST

RUBBER SERVICE DEPARTMENT, IMPERIAL CHEMICAL INDUSTRIES, LTD., BLACKLEY, MANCHESTER, ENGLAND

The increased use of the Mooney viscometer in America for checking the plasticity of different batches of synthetic rubber has led to a wider appreciation of the care which is necessary for accurate operation of this apparatus. A recent article[1] dealt fairly fully with most of the factors affecting results obtained with the Mooney viscometer. Some results obtained on the instrument at Blackley are extremely interesting and publication may help other users to avoid the trap of using Vistanex for calibration purposes. Vistanex is a stable material chemically, which is essential for a standard material, but other factors overcome this advantage and preclude its use. The mechanical method of calibrating the machine checks the spring at readings 0 and 100 and as long as the spring is not taken beyond its elastic limit there is no point in checking intermediate values. Vistanex gives a reading of 50 when tested at 100° C in the standard manner. It has been assumed that if a reading of 50 is obtained with Vistanex, the instrument must be working correctly. This view is wrong.

For correct operation the die closure must be such that uniform pressure is obtained at all points between the surfaces of the two dies. A method of checking this has been given by Taylor[1]. A series of results obtained at Blackley with GR-I were obviously wrong, although a reading of 50 was obtained with Vistanex. On investigating further, Vistanex was found to be insensitive to the die closure, whereas GR-I was extremely sensitive.

The following results were obtained with different die closures.

Die closure	Vistanex	GR-I
1. Correct die closure	50.5	45
2. High pressure on right side and low pressure on left side of die	50	27
3. Practically no pressure on left side of die	50	31
4. Very little pressure on right side of die	49.5	28
5. Intermediate between 1 and 2	50.5	40
6. Intermediate between 1 and 4	49.5	37

It appears, therefore, that Vistanex can give misleading results and its use for checking Mooney viscometers should be discontinued. The above results indicate that GR-I is a much more suitable material, but its adoption would depend on an adequate supply of material of a fixed plasticity. The alternative is to rely solely on the mechanical method of calibration and on Taylor's method of checking the die closure. Unfortunately the latter method depends to a great extent on the skill of the individual operator and, therefore, a check test with GR-I may still be desirable.

REFERENCE

[1]Taylor, *India Rubber World* 112, 582 (1945).

* Reprinted from the *India-Rubber Journal*, Vol. 109, No. 17, page 484, October 27, 1945.

RUBBER PLASTOMETER WITH UNIFORM RATE OF SHEAR—SHEARING-CONE PLASTOMETER *

G. H. Piper and J. R. Scott

Research Association of British Rubber Manufacturers, Croydon, England

INTRODUCTION

The plastic flow of unvulcanized rubber and other high polymers does not in general obey Newton's law that the rate of flow is proportional to the applied stress. The viscosities of these materials are a function of their rates of shear. For a complete knowledge of the plastic flow of these materials it is necessary to determine the rate of flow at various stresses, the effect of temperature, and, where thixotropic or other time effects are present, the effect of time of application of stress. The ideal plastometer, both for research and industrial control, should thus be capable of measuring the stress required to produce several definite rates of plastic flow, and of maintaining the stress constant so that time effects can be studied. Furthermore, if the instrument is used for factory control, the rates of flow should be of the same order as the rates met with in the factory processing of the material.

The plastometers in general use in the rubber industry suffer from one or more of the following disadvantages, as has previously been indicated more fully by one of the present authors[1].

(1) The rate of shear is not uniform throughout the material.

(2) As a result of (1), the fundamental plastic-flow relation is in general not obtainable; thus, in the parallel-plate plastometer the relation between shear rate and stress can only be obtained indirectly by a complicated mathematical treatment[2], which assumes *a priori* a power law or other simple relation between these quantities.

(3) The plasticity is measured at shear rates far removed from those encountered in processing. These processing rates in the rubber industry extend up to about 50/sec., the high rates occurring in extrusion machines, while the low rates are of interest for some technical problems, such as the distortion of thin extruded tubing under its own weight.

(4) The shear stress in the material under test does not remain constant.

The Mooney shearing-disk plastometer[3], which overcomes some of these disadvantages, has a rotating disk surrounded by the plastic material, and the torque required to rotate the disk at 2 r.p.m. is measured by the thrust on a shaft carrying a worm wheel which drives the shaft carrying the disk. The rate of shear is not uniform, but increases from zero near the center of the rotor to a maximum of 1.0/sec. at the edge. This rate is much nearer (though still below) rubber processing rates than those obtained in the parallel-plate or Williams plastometer, which are normally below 0.02/sec. A plastometer of the rotating cylinder type has also been described by Mooney[4]. This instrument is intended for research and not for industrial work, a range of shear rates

* Reprinted from the *Journal of Scientific Instruments*, Vol. 22, No. 11, pages 206–210, November 1945.

being obtained by altering the driving weights, the maximum being of the order 25–100/sec.

DESIGN OF THE PLASTOMETER

The plastometer developed by this Research Association has been designed to overcome these disadvantages, the chief features being the uniform rate of shear obtained by a special shape of rotor, and the provision of a wide range of shear rates. As the shearing action is produced by rotating conical surfaces, the instrument is termed a shearing-cone plastometer. The mechanical design of the plastometer, apart from the rotor and mould and the variable-speed drive, is based on the Mooney shearing-disk plastometer. The details of the rotor, mould, and other parts are shown in Figure 1. The rotor (1) is of mush-

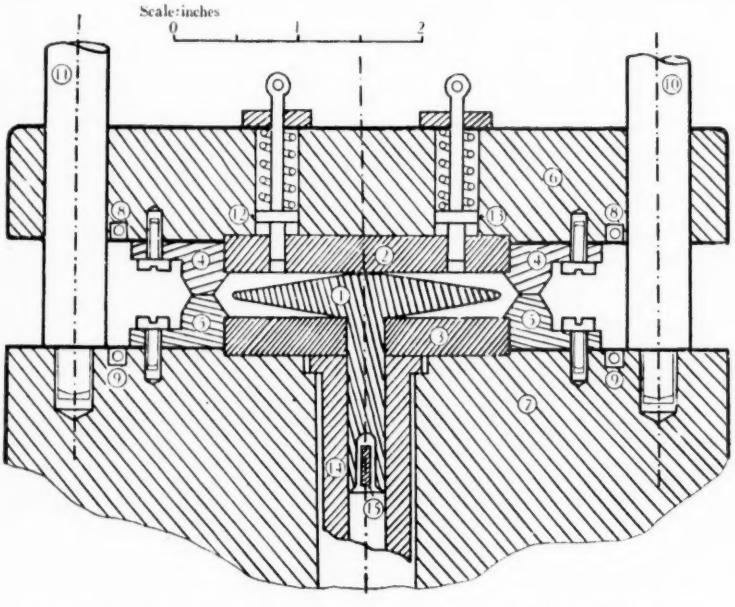

FIG. 1.—Shearing-cone plastometer; vertical section through platens, mould, and rotor.

room shape, the upper and lower surfaces being formed by two cones of large apex angle, the axis of rotation being the axis of the two cones. The rubber fills the space between the rotor and the stationary mould (2, 3, 4, 5); except at the edge, the rubber is thus sheared between the conical surfaces of the rotor and the flat walls of the mould (2, 3, Figure 1). The distance between the shearing surfaces here increases proportionally with the distance from the axis of rotation, and the rate of shear is thus uniform and equal to ω/α, where ω is the angular velocity of the rotor and is the angle between the two shearing surfaces.

The cylindrical mould in which the rotor is rotated is formed by the top and bottom surfaces of the circular dies (2) and (3) and the clamping rings (4) and (5). The dies (2) and (3) are clamped to the movable platen (6) and the fixed platen (7), respectively, so that the mould may be opened into two halves by raising the movable platen. The platens are heated electrically by the

embedded resistance coils (8) and (9), and their temperatures are individually controlled by two Sunvic thermostat units used with hot-wire relays. To reduce temperature oscillation the current in the platen coils is adjusted so as to give, in the absence of a cut-off, a slow rise in temperature past the temperature required, and an adjustable resistance is put across the contacts of the 'cut-off' so that when 'cut-off' occurs the current is reduced but not cut off completely. The temperature is thus kept constant to 1.0° C under normal conditions, while if the mould is kept closed during an experiment the variation may not exceed 0.2° C. To open and close the mould, the upper platen slides vertically along two pillars $5\frac{1}{2}$ inches apart (10, 11), the motion being effected by an Archimedean screw mechanism instead of the double-lever mechanism used in the Mooney plastometer.

The rotor (1) is driven by the rotating sleeve (14), which carries a key (15) that fits into a slot in the rotor shaft. The sleeve (14) is rotated by a worm gear giving a ratio 180:1. This ratio is used instead of the Mooney 90:1 ratio. The torque is measured, as in the Mooney plastometer, by means of the thrust on the shaft carrying the worm. The drive is from a synchronous electric motor giving 1500 r.p.m. and a gear box which gives four speeds of rotation of the rotor 12, 1.2, 0.12, and 0.012 r.p.m., corresponding to shearing rates in the rubber of 10, 1, 0.1 and 0.01/sec.

It may be noted here that with highly viscous materials like rubber, heat generation sets an upper limit to the feasible shear rates. A material of effective viscosity η_e (c.g.s. units) and specific heat H, sheared at a rate $d\sigma/dt$ (per sec.), rises in temperature by $\left(\frac{d\sigma}{dt}\right)^2 \cdot \frac{\eta_e}{HJ}$ (° C/sec.) if no heat is conducted away (J = mechanical equivalent of heat). With rubbers H = about 0.5 and η_e may be as high as 10^6, so that with $d\sigma/dt = 10$ this formula gives a temperature rise of about 5° C/sec.

The torque on the rotor shaft is indicated by a calibrated dial micrometer gauge which measures the endwise movement of the worm shaft against a steel cantilever spring. The dial gauge is calibrated by fixing a pulley on a shaft which is inserted into the sleeve in place of the rotor, and applying a torque by means of weights attached to a wire passing round the pulley. The dial gauge is read while the motor is running.

Dimensions of the rotor and mould were chosen so that the torque produced by the edge zone, where the shear rate is not uniform, would have only a small influence on the results. The dimensions (see Figure 2) are $EM = 1.0$ inch, $R_1 = 0.05$ inch, and $\alpha = 7°10'$ (=0.125 radian). The angle α should be as small as possible (see section on the *Determination of rheological constants from measurements of the total torque*, below), but a lower limit is set by mechanical difficulties. The intention originally was to give the edge walls of the mould the shape (semicircular in section) shown in Figure 2, but owing to the difficulty of machining grooves on the curved surface, the half-hexagon section shown in Figure 1 was adopted for the first trials. The difficulties of machining the shape shown in Figure 2 do not, however, appear insuperable.

The rotor is of hardened cast steel, and the conical surfaces are grooved with sharp 60° radial grooves, which extend over the entire shearing surface and edge and increase in depth from a minimum near the center of the rotor to a maximum at the edge, where the grooves are 0.05 inch apart. The effective surfaces of the upper and lower dies are cross-hatched as in the Mooney instrument, and the inner surfaces of the confining rings are grooved vertically with 24 grooves per inch. The mould is filled with rubber by first removing the

rotor and placing pieces of rubber above and below it, the lower piece being ring-shaped to accommodate the rotor shaft. The rotor is placed in position and the mould closed, excess rubber being forced out between the two halves of the mould and at a later stage into the cavities under the spring-loaded plungers (12) and (13). These plungers exert a pressure of 400–800 lbs. per sq. in. on the rubber, forcing it into intimate contact with the grooved shearing surfaces and preventing slipping.

The recovery or elastic retraction of unvulcanized rubber, especially synthetic rubber, has an important influence on its processing characteristics. It is intended at a later date to modify the instrument so as to measure recovery by incorporating a clutch mechanism in the drive and thus leave the rotor free to move as the rubber retracts. The related property of stress relaxation may be observed without modification of the instrument by keeping the electric

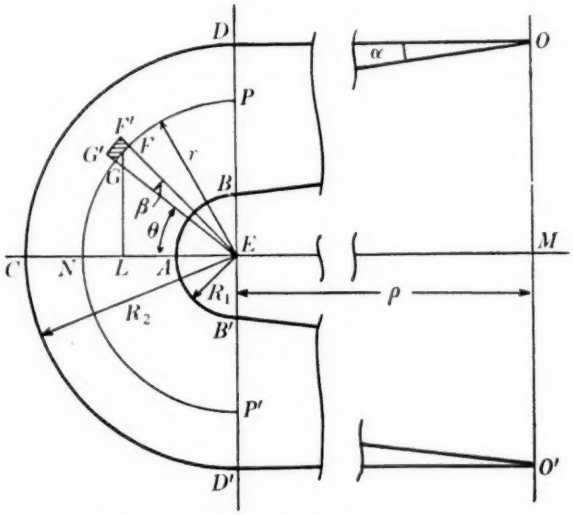

FIG. 2.—Vertical section of apparatus through the axis of rotation OMO', showing one-half of the mould $ODCD'O'$ and of the rotor $OBAB'O'$.

motor stationary and rapidly turning the horizontal shaft carrying the worm a few revolutions so that the required torque is set up, or alternatively by stopping the motor after a normal test run. The decay of this torque with time is measured by the dial gauge, and the method may be considered valid as long as the displacement of the spring and worm shaft produced by the torque is small. Some results on the stress relaxation of masticated rubber have been obtained by this method.

OPERATION AND EXPERIENCE WITH THE PLASTOMETER

The normal procedure has been as follows. After putting the cold rubber in the mould, the latter is closed after a minute's heating, and the motor is switched on to give a rotor speed of 1.2 r.p.m. A constant reading is reached in 4–5 minutes. The rotor is then driven at the other speeds of 0.12, 0.012, and 12 r.p.m. successively, and the corresponding readings are taken. During the first 4–5 minutes the rubber is heating up, and entrapped air works out of the

mould; for subsequent readings less time is required. The whole operation takes about 15 minutes.

The chief difficulty experienced has been the fluctuating values shown by the dial indicator gauge. These have been of two types: (1) fluctuations corresponding to each revolution of the worm shaft, (2) fluctuations corresponding to each revolution of the rotor shaft. The former may be due to incorrect meshing of the gears, or to the end of the worm shaft not being perfectly flat where it contacts the stem of the dial gauge. The second type has been the chief difficulty, and after considerable experiment the following conclusions were drawn. The fluctuations were due to fluctuating friction caused by eccentricity in rotation of the rotor; this eccentricity developed when the rotor was under load, and was due to the slot in the rotor and the key (15) not being truly central, the rotor shaft thus being forced a few thousandths of an inch to one side of the sleeve, in which it necessarily has a definite though small clearance. The slot was therefore made dead true, and the key moved down to the position shown from its original position near the top of the sleeve, with the result that the fluctuations were finally reduced to 3 per cent of the measured torque. The position of the lower die also needs to be adjusted laterally, to the extent of a few thousandths of an inch, until the fluctuations are reduced to their lowest possible value.

Previous experiments showed that there was a tendency for rubber to creep down between the rotor shaft and the lower die, and this increased the magnitude of the fluctuating friction. Reducing the clearance between shaft and lower die, however, increased the fluctuations because of the increased viscous friction.

It is not considered that finality has been reached in the design. The method of transmitting the torque to the rotor is not considered satisfactory; an improvement might be the use of an Oldham universal coupling. The creep of rubber down the shaft, which occurs also in the original Mooney shearing-disk plastometer, and is noticeable mainly with soft rubbers, should be prevented. Partial prevention of the creep would, however, be useless, as this would introduce an uncertain viscous friction.

THEORY OF THE SHEARING-CONE PLASTOMETER

Let α = angle between the two main shearing surfaces
ω = angular velocity of the rotor
σ = shear strain
t = time
$\dot{\sigma} = d\sigma/dt$ = rate of shear
$\dot{\sigma}_u$ = rate of shear in the uniform zone (nominal rate of shear)
s = shear stress
s_u = shear stress in the uniform zone
n = exponent in the assumed stress/flow relation (1)
η' = consistency of the material, in relation (1)
R_1 = edge radius of the rotor (see Figure 2)
R_2 = edge radius of the mould (see Figure 2)
ρ = radius of conical part of the rotor
T_u = torque due to the uniform zone, *i.e.*, to forces acting on OB and $O'B'$ (Figure 2)
T_e = torque due to the edge zone, *i.e.*, to forces acting on BAB' (Figure 2)
T = total torque ($= T_u + T_e$)

r = distance of surface element FG from the center E (Figure 2)
θ = angle GEC (Figure 2)
β = angle FEG (Figure 2)
ω' = angular velocity of surface element FG about the axis OMO' (Figure 2)
$d\omega'$ = increment corresponding to a small increment dr
X = an expression (8) which is an instrumental constant for Newtonian or pseudoviscous materials

The experimentally observed quantities are the torque and the angular velocity of rotation of the rotor, while the quantities required are the absolute shear stress and the corresponding rate of shear.

The material above and below the rotor is uniformly sheared, and the stress and rate of shear are uniform at a fixed rate of rotation, so the torque produced is directly proportional to the stress. The stress and shear rate in this uniform zone (ODB and $O'D'B'$, Figure 2) will be termed the nominal stress and nominal rate of shear. To simplify the mathematical treatment, the cross-section of the edge of the mould (DCD') has been given the ideal semicircular form, instead of the half-hexagon shape actually used. The rate of shear in the edge zone ($DCD'B'AB$) and the corresponding stress are not uniform, and decrease with increase in distance from the center E, and as the torque due to the edge zone is not inappreciable, the experimentally observed total torque cannot be assumed to be simply related to the nominal stress. The relation is derived below (Equation (10)); it is shown that the error introduced by assuming that the total torque is proportional to the nominal stress is small if the dimensions of rotor and mould are chosen correctly, and the best values of these dimensions are calculated.

It will first be assumed, to facilitate the treatment, that the plastic flow follows the general relation:

$$d\sigma/dt = (s/\eta')^n \tag{1}$$

where η' and n are constants for a given material.

Torque due to uniform zone.—It can readily be shown that in this zone the rate of shear $d\sigma/dt = \omega/\alpha$, and hence that

$$T_u = 5\pi\rho^3\eta'(\omega/\alpha)^{1/n} \tag{2}$$

Torque due to edge zone.—In the edge zone the flow is much more complex, but an approximate expression for the torque is derived as follows:

We may consider the material in the edge zone as moving in the form of imaginary laminae round the axis of rotation OMO' (Figure 2), the material in any one lamina having a fixed angular velocity. $PFGNP'$ represents a cross-section through such a lamina by a plane passing through OMO', the axis of rotation, and the assumption is made that $PFGNP'$ is semi-circular with center E. This assumption would be strictly true if the radius ρ were infinitely large, so that the system resembled the case of material sheared between two concentric cylinders, one moving axially within the other; since ρ is actually finite, the assumption becomes an approximation.

Let $GFF'G'$ be a small annular element at a distance r from the center E and having a thickness dr. Let angle $GEN = \theta$, the very small angle $FEG = \beta$, the angular velocity of surface $GF = \omega'$, and angular velocity of $G'F' = \omega' + d\omega'$, about axis OMO'.

Then the rate of shear in the element is given by:

$$\frac{d\sigma}{dt} = \frac{(\rho + r\cos\theta)d\omega'}{dr} \tag{3}$$

where $(\rho + r\cos\theta)$ is the distance (LM) of the element from the axis OMO'.

Let dT_e be the torque (about OMO') produced by the shear stress acting at the surface (FG) of the element. Then:

$$dT_e = 2\pi(\rho + r\cos\theta)^2 r\beta\eta'(d\sigma/dt)^{1/n}$$

or substituting from (3):

$$= 2\pi(\rho + r\cos\theta)^{2+1/n} r\beta\eta'(d\omega'/dr)^{1/n}$$

Hence

$$\omega = \int_{R_1}^{R}\left(\frac{d\omega'}{dr}\right)dr = \left(\frac{dT_e}{2\pi\beta\eta'}\right)^n \int_{R_1}^{R_2} \frac{dr}{r^n(\rho + r\cos\theta)^{2n+1}} \tag{4}$$

(The assumption, implicit in Equation (4), that dT_e is independent of r, though not strictly true, is an adequate approximation.)

In practice r is much less than ρ, hence the term in brackets in the denominator of the integral may be expanded binomially and, provided n is of the order of unity, all terms after the second can be neglected; integration then gives:

$$\omega = \left(\frac{dT_e}{2\pi\beta\eta'}\right)^n \left\{\frac{R_1^{1-n} - R_2^{1-n}}{(n-1)\rho^{2n+1}}\right\} \times \left\{1 - \frac{(n-1)(2n+1)(R_1^{2-n} - R_2^{2-n})\cos\theta}{(n-2)\rho(R_1^{1-n} - R_2^{1-n})}\right\} \tag{5}$$

Since the second term in the right-hand bracket is much less than unity, Equation (5) may be rearranged to give, as a first approximation:

$$dT_e = 2\pi\eta'\omega^{1/n}\rho^{2+1/n}\left(\frac{n-1}{R_1^{1-n} - R_2^{1-n}}\right)^{1/n} \times \left\{1 + \frac{(n-1)(2n+1)(R_1^{2-n} - R_2^{2-n})\cos\theta}{n(n-2)\rho(R_1^{1-n} - R_2^{2-n})\cos\theta}\right\}\beta \tag{6}$$

Replacing β by $d\theta$ and integrating with respect to θ, between the limits $+\frac{1}{2}\pi$ and $-\frac{1}{2}\pi$, finally gives:

$$T_e = 2\pi^2\eta'\omega^{1/n}X \tag{7}$$

where, in general:

$$\left.\begin{aligned} X &= \rho^{2+1/n}\left(\frac{n-1}{R_1^{1-n} - R_2^{1-n}}\right)^{1/n} \times \left\{1 + \frac{2(n-1)(2n+1)(R_1^{2-n} - R_2^{2-n})}{\pi n(n-2)\rho(R_1^{1-n} - R_2^{1-n})}\right\} \\ \text{or, if } n = 1: \quad X &= \frac{\rho^3}{ln(R_2/R_1)}\left\{1 + \frac{6(R_2 - R_1)}{\pi\rho ln(R_2/R_1)}\right\} \\ \text{or, if } n = 2: \quad X &= \rho^{5/2}\left(\frac{1}{R_1^{-1} - R_2^{-1}}\right)^{1/2}\left\{1 + \frac{5ln(R_2/R_1)}{\pi\rho(R_1^{-1} - R_2^{-1})}\right\} \end{aligned}\right\} \tag{8}$$

It will be seen that X depends only on n and on the dimensions of the instrument.

For values of n as high as 10, the approximations used in deriving Equations (5) and (6) are not mathematically valid, because the third and subsequent terms in the binomial expansion of $(\rho + r\cos\theta)^{2n+1}$ are not negligible, and the second term in the right-hand bracket of (5) may be comparable with unity. Nevertheless, as can be shown by numerical examples, these approximations do not lead to serious error; thus, in the extreme case where $n = 10$, $R_1 = 0.254$ cm., and $\alpha = 0.125$ radian, the error in T_e is only 1.2 per cent and in T/s_u only 0.5 per cent.

Determination of rheological constants from measurements of total torque.— From (2) and (7) the total torque $T(= T_u + T_e)$ is given by:

$$T = 5\pi\rho^3\eta'(\omega/\alpha)^{1/n} + 2\pi^2\eta'\omega^{1/n}X \tag{9}$$

where X has the value given by Equation (8).

If the material under test obeys the power law of Equation (1), varying ω does not affect any other quantity on the right-hand side of Equation (9); hence T is proportional to $\omega^{1/n}$, and n can thus be determined from the slope of the low ω/log T curve (actually a straight line). When n is known, X can be evaluated from Equation (8) and inserted in Equation (9) to give η'. In this case the total torque T is proportional to the stress in the uniform zone, since this equals $\eta'(\omega/\alpha)^{1/n}$.

If the material does not obey the simple power law, the log ω/log T curve is not straight, in other words there is no unique value of n.

In the general case the stress/shear-rate relation can be written $s = \phi(d\sigma/dt)$, where ϕ is the function to be determined. If we had to consider only the uniform zone, the problem would be simple, because $d\sigma/dt = \omega/\alpha$, and the stress in this zone (s_u) is proportional to the corresponding torque T_u ($=\frac{4}{3}\pi\rho^3 s_u$). The edge zone, however, disturbs this simple proportionality between stress and torque, as the following considerations show.

For all probable forms of ϕ, the relation between stress and shear rate may be written as a modification of Equation (1), *viz.*, $s = \rho'(d\sigma/dt)^{1/n}$, where η' and n are now functions of $(d\sigma/dt)$ and hence of ω. Since $s_u = \eta'(\omega/\alpha)^{1/n}$, Equation (9) can be written:

$$T = \tfrac{4}{3}\pi\rho^3 s_u + 2\pi^2 s_u X\alpha^{1/n} \tag{10}$$

If ω is varied, this alters the value of n and hence of $X\alpha^{1/n}$, so T no longer remains proportional to s_u. It therefore becomes necessary to know how far T deviates from proportionality to s_u (*i.e.*, how much T/s_u varies) as n changes, and also how the extent of this deviation depends on the dimensions of the instrument.

Since the shear rate is not uniform throughout the edge zone, η' and n do not have single fixed values, but as a first approximation we may assume values corresponding to the shear rate in the uniform zone, which approximates to the mean shear rate in the edge zone (it can be shown that this assumption does not invalidate the estimate of the overall variation of T/s_u with ω).

It is evident from Equation (10) that a small value of α is advantageous, since this reduces $X\alpha^{1/n}$ and hence its variation with n (Table 2 confirms this quantitatively). Using Equation (8) to calculate X, and taking the value of ρ actually adopted (1.00 inch), gives the results shown in Tables 1 and 2, where T is expressed as dyne-cm. and s_u in dynes per sq. cm.

The best dimensions (R_1 and α) are those for which the proportionate variation of T/s_u with change of n is least; Table 1 thus shows that the value of R_1 is not critical, while Table 2 shows that α should be small. A variation of n between 0.5 and 10 with changing shear rate represents a very extreme case, whence it may be concluded that in general the ratio T/s_u remains reasonably constant as ω is varied. Consequently the curve of log T against log ω has

TABLE 1

α CONSTANT (=0.125 RADIAN); R_1 VARYING

R_1	n	T/s_u cm.³	T/s_u relative to the n = 2 value as unity
0.0254 cm. (=0.01 in.)	0.5	89.0	1.10
	2	81.1	(1.00)
	10	73.9	0.91
0.127 cm. (=0.05 in.)	0.5	111.0	1.075
	2	103.1	(1.00)
	10	92.4	0.895
0.254 cm. (=0.10 in.)	0.5	139.6	1.085
	2	128.5	(1.00)
	10	116.0	0.905

TABLE 2

R_1 CONSTANT (=0.127 CM.); α VARYING

α Radian	n	T/s_u cm.³	T/s_u relative to the n = 2 value as unity
0.05	0.5	96.6	1.03
	2	94.0	(1.00)
	10	90.3	0.96
0.125	0.5	111.0	1.075
	2	103.1	(1.00)
	10	92.4	0.895
0.20	0.5	125.7	1.135
	2	110.6	(1.00)
	10	93.5	0.845

very nearly the same shape as that of log s_u against log ω or log $\dot{\sigma}_u$ (where $\dot{\sigma} = d\sigma/dt$), since the nominal shear rate σ_u is proportional to ω. This shape in itself gives valuable information on the rheological character of the material. To complete the evaluation we use the fact that the inverse slope of this curve, *i.e.*, $d \log \omega/d \log T$, at any point gives an approximate value for n (which would be given exactly by $d \log \dot{\sigma}_u/d \log s_u$), so it is easy to read off, at various values of ω, the corresponding values of n and hence calculate values for X and finally (from Equation (10)) for s_u; since $\dot{\sigma}_u = \omega/\alpha$, we thus obtain a series of corresponding values for shear stress (s_u) and shear rate ($\dot{\sigma}_u$), which can be plotted to give the fundamental flow curve of the material, *i.e.*, the function ϕ.

RESULTS OBTAINED WITH THE SHEARING-CONE PLASTOMETER

Typical curves obtained with the apparatus are shown in Figure 3 for (1) well-masticated natural rubber, (2) masticated GR-S synthetic rubber (butadiene-styrene copolymer). There is no linear relation between stress and rate of shear, and over the range of shear rates investigated the results follow the simple power law of Equation (1).

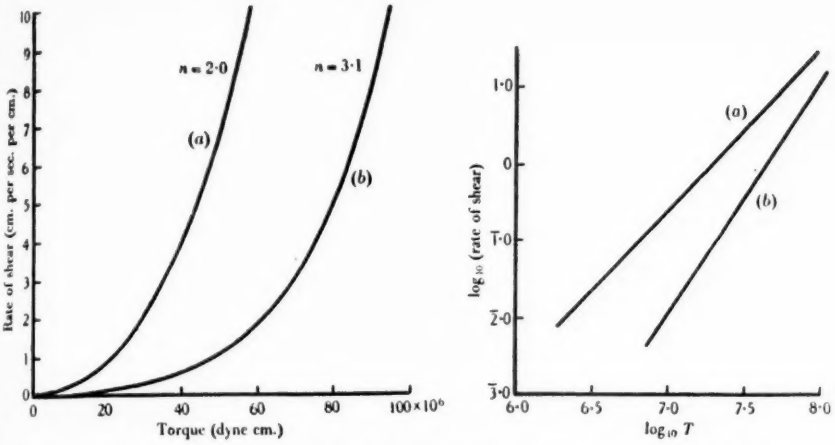

FIG. 3.—Typical curves showing relation between torque and rate of shear: (*a*) natural rubber, (*b*) synthetic rubber (GR-S).

ACKNOWLEDGMENT

The authors wish to thank the Research Association of British Rubber Manufacturers for permission to publish this paper.

SUMMARY

A new shearing-cone plastometer, suitable for investigating the plastic-flow relations of highly viscous materials over a wide range of stress, is described. A mushroom-shaped rotor, having upper and lower surfaces of conical type, is rotated in the plastic material contained in a cylindrical mould. With this type of shearing surface the rate of shear is uniform throughout the material, except for a small edge zone, thus overcoming some disadvantages of previous plastometers. The mechanical design is based on the Mooney shearing-disk plastometer except that provision is made for a wide range of speeds of rotation.

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QUALITATIVE SPOT TESTS FOR RUBBER POLYMERS *

H. P. BURCHFIELD

NAUGATUCK CHEMICAL DIVISION OF THE U. S. RUBBER CO., NAUGATUCK, CONN

To eliminate processing difficulties and ensure the production of standard natural and synthetic rubber reclaims, the scrap used as the raw material must be carefully segregated. When mold markings are lost, or large consignments of miscellaneous scrap are received, methods for distinguishing between the basic polymers are necessary.

This paper describes a new color reaction which will serve to characterize natural rubber, GR-S, and Perbunan. Confirmatory tests included in the same operation distinguish between the remaining commercially important types. The procedure is sufficiently rapid to be practical in the testing of representative samples from carload shipments, or for establishing the identity of materials on which indecisive results are obtained by less specific methods.

For the routine assortment of scrap, spot tests are proposed, which are carried out by holding impregnated filter paper strips in the smoke emitted when the sample is branded with a metal rod heated to redness. Color changes take place which indicate the nature of the polymer. One test distinguishes between natural rubber and GR-S; a second is specific for Butyl; a third differentiates Neoprene-GN, Neoprene-ILS, and Perbunan from one another and from the hydrocarbon rubbers. The spot reactions can be carried out very rapidly, and are particularly useful when large numbers of samples must be examined.

Several laboratory methods for the identification of the components of mixtures are discussed. Although they require too much time for routine testing, they are of value in the examination of special samples.

In a previous publication[1] a procedure for the identification of natural and synthetic rubbers was described. The test depends primarily on an approximate determination of the pH and specific gravity of the products obtained by destructive distillation of the sample. Although the method is adequate in many applications, the inclusion of color tests to distinguish the hydrocarbon rubbers is desirable. The difference in specific gravity between pyrolyzates obtained from natural rubber and GR-S is small, and to reproduce the test requires carefully controlled experimental conditions, and occasionally a preliminary extraction to remove organic compounding ingredients.

As reactions can be carried out more conveniently on the pyrolyzates than on the original materials, these were first investigated to obtain sufficiently rapid tests for plant control work. Although GR-S contains aromatic nuclei, and natural rubber is purely aliphatic, this distinction does not apply to their pyrolyzates, for although the primary decomposition products of rubber are isoprene and dipentene, a number of aromatics are produced through secondary reactions[2]. A more rapid and definite distinction can be made by reacting the pyrolyzates with substances capable of condensing with compounds containing labile hydrogen atoms. Of the reagents investigated, *p*-dimethylaminobenz-

* Reprinted from Industrial and Engineering Chemistry, Analytical Edition, Vol. 17, No. 12, pages 806–810, December 1945.

aldehyde was found to be the most effective; it yields colored condensation products with the distillates from a number of polymers, which are sufficiently characteristic to serve as criteria of identity.

The reaction is carried out by distilling the pyrolyzate from a rubber sample into a dilute alcoholic hydrochloric acid solution of the aldehyde. An initial color is produced which is intensified and altered by diluting the reaction mixture with methanol and heating on a water bath. The distillate from natural rubber produces an intense violet-blue, and that from GR-S a green. Perbunan yields a red product, Neoprene a yellow-green, and Butyl a blue-green of comparatively low intensity.

The pyrolysis test previously described[1] has been rearranged to include the aldehyde reaction. The indicator and buffer systems are completely revised, but accomplish essentially the same purpose as those described in the earlier paper. The alkalinity test for Perbunan and the drop test for natural rubber are omitted, since the aldehyde reaction is more specific.

Solution I contains *p*-dimethylaminobenzaldehyde in dilute alcoholic hydrochloric acid, to which hydroquinone is added as a stabilizer. The specific gravity is adjusted to 0.851 with ethylene glycol, so that Butyl rubber can be distinguished from the other polymers by the low density of its pyrolysis product. Solution II contains Metanil yellow and bromocresol green in a citrate buffer. The initial color is green, which changes to yellow in the presence of acetic acid and to red in the presence of hydrochloric acid. These color changes are used for distinguishing polymers which yield organic acids and those which contain chlorine from one another, and from materials which give neutral or alkaline products on decomposition.

In place of the previously specified heating element and quartz tubes, 10 × 75 mm. soft glass test-tubes heated with a microburner are employed. This is made possible by the fact that the color tests do not vary so widely with respect to experimental conditions as the drop tests. The tubes are inexpensive and can be discarded after one use. In addition to the added speed and convenience of making the tests, a smaller sample is required, which is often of importance in the analysis of surface coatings or other materials which are available only in small quantities and must be laboriously removed from the supporting fabric.

Table I describes the reactions which occur when the decomposition products from the compounded polymers are distilled into the test solutions. In the case of the aldehyde reaction, both the initial color and that obtained after

TABLE I.

PYROLYSIS TESTS

Material	Solution I		Solution II, Color
	Initial color	Color after heating	
Blank	Pale yellow	Pale yellow	Green
Polyvinyl chloride	Yellow	Yellow	Red
Neoprene-GN	Yellow	Pale yellow green	Red
Neoprene-ILS, Neoprene-Perbunan mixtures	Orange red	Red	Yellow to red
Perbunan	Orange red	Red	Green
GR-S	Yellow green	Green	Green
50 GR-S-50 rubber	Olive green	Green blue	Green
Natural rubber	Brown	Violet blue	Green
Butyl	Yellow (droplet floats)	Pale blue green	Green
Polyvinyl acetate	Yellow	Pale yellow green	Yellow

dilution and heating are listed. The table includes the types in most common use, and two simple mixtures, in which both components are present in considerable amounts.

REAGENTS

Solution I.—Dissolve 1.0 gram of *p*-dimethylaminobenzaldehyde and 0.01 gram of hydroquinone in 100 cc. of absolute methanol. Add 5 cc. of concentrated hydrochloric acid and 10 cc. of ethylene glycol. Adjust the specific gravity to 0.851 at 25°/4° C by the addition of a calculated amount of solvent. The reagent is stable over a period of several months when stored in a brown bottle.

Solution II.—Dissolve 2.00 grams of sodium citrate, 0.20 gram of citric acid, 0.03 gram of bromocresol green, and 0.03 gram of Metanil yellow in 500 cc. of distilled water.

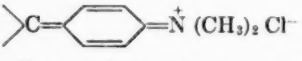
PROCEDURE

Place approximately 0.5 gram of the sample in a 10 × 75 mm. test-tube and attach a 4-mm. outside diameter side arm by means of a cork. Suspend the tube by a wire from a ring stand and heat with a microburner until the sample begins to decompose. Avoid localized overheating to prevent softening of the glass.

When vapors appear at the mouth of the side arm, immerse the end beneath the surface of 1.5 cc. of Solution II contained in a 10 × 75 mm. tube. After it is evident whether a color change will take place or not, remove the tube and continue the distillation into 1.5 cc. of solution I. Permit the tubes to cool for a minute or two and shake. Note the position of the droplet in Solution I and the color changes which take place. Transfer Solution I to a 16 × 150 mm. test-tube and add 5 cc. of absolute methanol. Heat on a water bath at 100° C for 3 minutes and note the color which develops. A description of the reactions obtained is given in Table I.

If the absence of other interfering polymers has been established by the above test and the principal interest lies in the detection of natural rubber and GR-S, repeat the experiment on a 0.2- to 0.3-gram chloroform-extracted sample. Collect the total distillate under 1.5 cc. of Solution I and note the color of the solution before and after heating. If a blue-green to green-blue color is obtained, it is probable that the sample is a rubber—GR-S mixture or a natural rubber reclaim. Test for the presence of crude rubber by the Weber method[1], and if necessary confirm the presence of GR-S by the coupling procedure[3].

p-Dimethylaminobenzaldehyde has been used for the colorimetric estimation of pyrrole[4], indole[5], methol[6], and a number of biological materials. The reaction with pyrrole depends on the formation of a pyrrolenine compound which gives a deep red color in hydrochloric acid solution[7]. No attempt has been made to isolate those compounds in the pyrolyzates of the elastomers which give rise to the colored products. However, it is evident that the reaction depends on the production of compounds containing labile hydrogen atoms which react with the aldehyde with the elimination of water to form colored salts of the type:



On the addition of alkali the solutions become yellow, but on acidification the initial colors reappear. On prolonged standing fading takes place. This is particularly noticeable in the case of natural rubber, where the solution changes from violet-blue to violet during the course of a few hours.

Absorption curves of the reaction products of the pyrolyzates obtained from vulcanized chloroform-extracted samples are shown in Figures 1 and 2. The optical measurements were made with a Beckman spectrophotometer, and the specific extinction coefficients calculated from the weights of the distillates and the dilutions employed. The curve for natural rubber exhibits a maximum at 550 mμ, and that for GR-S a maximum of approximately one-half the intensity at 620 mμ. Composite curves are obtained on mixtures of the two polymers, the shape of the curve depending on the percentage composition. The reaction product obtained from Perbunan has an intense band at 540 mμ, while that from Neoprene absorbs weakly at 540 and 635 mμ. The curves are not quantitatively reproducible, but the differences in absorption between the products obtained from the various polymers are sufficient to allow for accurate identification over a wide range of compounding.

The wave lengths at which maximum absorption takes place are independent of the state of cure, although in general more intense colors are obtained from vulcanizates than from crude polymers. A series of natural rubber samples in which the sulfur content was varied from 1.5 to 12 parts produced colors differing only in intensity from that obtained from pale crepe.

By making absorption measurements at 550 and 620 mμ on the qualitative test solutions obtained in the analysis of natural rubber, GR-S, and Perbunan, density ratio values characteristic of the polymers can be obtained. These serve as numerical indexes of the reproducibility of the test and can be used in the evaluation of interfering substances. If the measurements are made on solutions of the same concentration at both wave lengths, the ratio of the optical densities will be independent of absolute concentration if the validity of the Beer-Lambert law is assumed.

$$R = \frac{\left(\log \frac{I_0}{I}\right) 550}{\left(\log \frac{I_0}{I}\right) 620}$$

Measurements made on a series of diluted test solutions with a Lumetron colorimeter, using monochromatic filters of 30 mμ band width, indicate that the density ratio varies from 0.7 to 0.8 for GR-S, from 1.3 to 1.6 for natural rubber, and from 2.8 to 3.3 for Perbunan. Intermediate values are obtained on mixtures and reclaims.

Typical ratios obtained on extracted and unextracted samples are shown in Table II. Each value represents the average of four independent determina-

TABLE II.
DENSITY RATIO VALUES OF QUALITATIVE TEST SOLUTIONS

Composition	R (extracted)	R (unextracted)
Crude Perbunan	..	3.21
Compounded Perbunan	3.18	2.83
Reclaimed Perbunan	2.56	2.04
Pale crepe	..	1.46
Compounded rubber	1.42	1.43
Carcass reclaim	1.23	1.30
Grade F camelback	1.11	1.10
50 rubber-50 GR-S	1.14	1.10
Grade C camelback	0.90	0.89
Crude GR-S	..	0.74
Compounded GR-S	0.74	0.72
Grade A camelback	0.73	0.73
GR-S reclaim	0.82	0.75

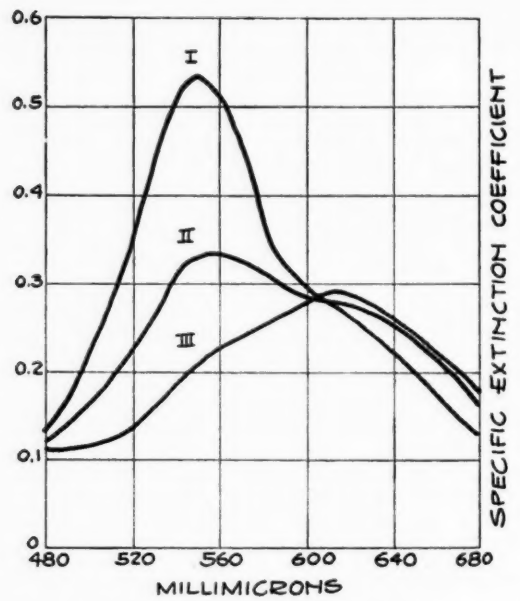


FIG. 1.—Absorption Spectra of *p*-Dimethylaminobenzaldehyde Reaction Products with Polymer Pyrolyzates

I. Natural rubber. II. 50–50 rubber—GR-S mixture. III. GR-S

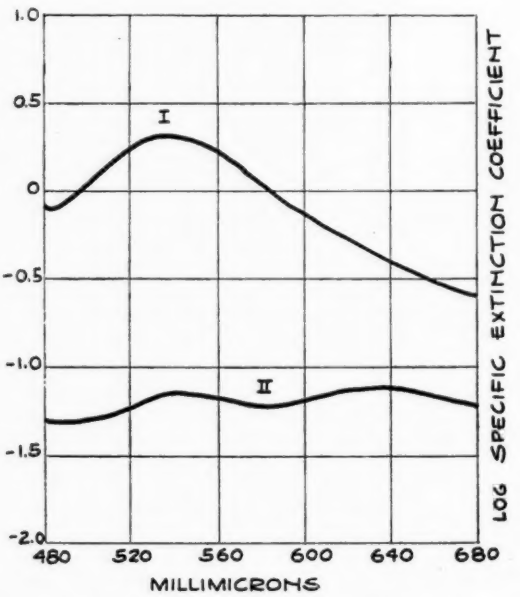


FIG. 2.—Absorption Spectra of *p*-Dimethylaminobenzaldehyde Reaction Products with Polymer Pyrolyzates

I. Perbunan. II. Neoprene

tions on the same sample. The standard deviations are 0.11 for Perbunan, 0.04 for natural rubber, and 0.02 for GR-S. While chloroform extraction may result in a change in ratio, the change is usually not great enough to alter the color of the solution.

It can be shown that the density ratio of the solution obtained from a binary mixture can be calculated from the percentage composition and the relative extinctions of the components, providing it is assumed that the reactive constituents are produced in the same proportions in which the polymers occur in the sample. Where K_λ and L_λ are the relative specific extinction coefficients of natural rubber and GR-S, and P is the percentage GR-S, this equation takes the following form:

$$R = \frac{100\,K_{550} + P\,(L_{550} - K_{550})}{100\,K_{620} + P\,(L_{620} - K_{620})}$$

If a value of unity is arbitrarily assigned to K_{550}, the remaining constants can be evaluated from the density ratios of solutions prepared from the pure materials and a mixture of known composition. While the reproducibility of the test does not justify an exact method of calculation, the relationship is useful in establishing the range of applicability of the color reaction. If a density ratio difference of 0.2 is the smallest which can be visually observed, it can be calculated that the limit of detection of GR-S in the presence of natural rubber is about 35 per cent, while the limit of detection of natural rubber in the presence of GR-S is about 20 per cent.

SPOT TESTS

When time is not an important factor, the pyrolysis procedure described above is recommended. However, when large numbers of samples must be tested, the use of spot methods has been found convenient. The general procedure is to dip a prepared indicator paper into a wetting solution and hold it in the smoke which is emitted when the sample is branded with a metal rod heated to redness. A characteristic color reaction is obtained in 4 to 6 seconds.

For the detection of Neoprene and Perbunan, the papers are impregnated with Metanil yellow and cupric acetate, and dipped in an alcoholic solution of benzidine dihydrochloride before use. If the polymer contains chlorine, a red color is produced by the action of the liberated hydrochloric acid on the acid-base indicator. This ordinarily serves as a test for Neoprene or polyvinyl chloride, although other chlorine-containing polymers give similar results. If the sample is Perbunan or a polymer containing nitrile nitrogen, a green color appears due to the presence of cyanide radicals in the decomposition products. This reaction, which takes place in the presence of benzidine and copper acetate, has been widely used for the detection of hydrocyanic acid in air[8]. The color is normally blue but is modified to a green by the color of the acid-base indicator. If substantial amounts of both chlorine and nitrile nitrogen are present as in Neoprene ILS, and Neoprene-Perbunan mixtures, both colors appear in bands on the filter paper strip, the green color appearing on the wet zone, and the red color most prominently on the dry portion of the paper. In the presence of the hydrocarbon rubbers no color changes are observed, although the paper may darken on drying. The presence of GR-S or natural rubber in admixture with either of these types does not alter the results obtained by the test, but the appearance of the colors may be delayed by dilution of the active constituents.

Butyl rubber is distinguished from natural rubber and GR-S by the use of blank filter paper strips which are immersed in a solution of mercuric sulfate in dilute sulfuric acid before making the tests. The pyrolyzate obtained from Butyl yields a brilliant yellow color; rubber and GR-S produce dull browns. The test depends on the presence of isobutylene in the decomposition products, which reacts with mercuric sulfate to form a complex with empirical formula[9] corresponding to $C_4H_8(HgSO_4 \cdot HgO)_3$.

The most useful test in the series is that which distinguishes natural rubber from GR-S. The materials required are prepared indicator paper strips impregnated with *p*-dimethylaminobenzaldehyde, and a 30% solution of trichloroacetic acid in isopropanol. A strip of indicator paper is dipped in the acid solution and held in the smoke emitted when a hot rod is held against the surface of the polymer. Rubber produces an intense blue coloration and GR-S a green. Mixtures containing equal parts of the two substances test as GR-S, although the green may be modified to a blue green. Samples containing 25 parts and less of GR-S test as natural rubber. The principal difficulty is caused by indecision in the classification of mixtures. The test is of value only for distinguishing GR-S from natural rubber, as the other polymers also give color reactions. While by careful observation, it is possible to distinguish some of the other types, more specific tests are preferred. Butyl produces a blackish coloration which fades to a pale lavender on standing 3 to 4 minutes. Perbunan produces a green color, but if the paper is held close to the heating unit until dry, a reddish brown spot appears. Neoprene gives a reaction almost indistinguishable from that of GR-S. Although the reaction is not specific, it may be used without supporting tests in many instances where it is only necessary to distinguish between natural rubber and GR-S.

A summary of the reactions obtainable by use of the spot tests is shown in Table III. If the origin and most probably composition of the sample are

TABLE III

SPOT TESTS

	Neoprene-Perbunan Test	Butyl Test	Rubber—GR-S Test
Neoprene-GN	Red	....	....
Perbunan	Green	....	....
Neoprene-ILS, Neoprene-Perbunan mixtures	Red/green	....	....
Butyl	Blank	Yellow	....
Natural rubber	Blank	Brown	Blue
GR-S	Blank	Brown	Green

unknown, the pyrolysis procedure is recommended. However, if a distinction must be made between a limited number of possibilities, the spot tests offer definite advantages with regard to economy of time and ease of manipulation.

APPARATUS

The tests can be conveniently carried out by use of a triangular file heated to redness in a Bunsen flame. When large numbers of samples are to be tested or where the presence of an open flame is undesirable, an electrically heated nickel-chromium knife can be employed. Units adaptable to the purpose are available from the Sta-Warm Electric Company, Ravenna, Ohio. The blade should be curved so that it can be easily applied to the surface of the rubber and

the end filed to a width of about 1 cm. to decrease the heating area and increase the temperature. When operated at a dull red heat, a test can be obtained in 4 to 6 seconds. The organic residue burns off between applications, and the inorganic deposit which slowly accumulates can be scraped off with a file.

INDICATOR PAPERS AND REAGENTS

Neoprene-Perbunan Test.—Dissolve 2.0 grams of cupric acetate and 0.25 gram of Metanil yellow in 500 cc. of methanol. Impregnate filter paper squares with the solution, dry, and cut into strips. Dissolve 2.5 grams of benzidine dihydrochloride in a mixture of 500 cc. of methanol and 500 cc. of water. Add 10 cc. of a 0.1 per cent aqueous solution of hydroquinone. Store in a brown bottle. A precipitate forms on standing, but if the solution is protected from light and air, it can be used for several months.

Butyl Test.—Use blank filter paper strips. To prepare the wetting solution, add 5.0 grams of yellow mercuric oxide to a mixture of 15 cc. of concentrated sulfuric acid and 80 cc. of water. Bring to a boil and continue heating until the oxide dissolves. Cool and make the volume up to 100 cc. with water.

Rubber—GR-S Test.—Impregnate filter paper squares with a solution of 3 grams of *p*-dimethylaminobenzaldehyde and 0.05 gram of hydroquinone in 100 cc. of ethyl ether. Dry and cut into strips. Papers stored in brown glass bottles show no discoloration and retain their activity after several weeks' storage. On prolonged storage under adverse conditions, the aldehyde oxidizes and the tests become progressively less distinct. To prepare the wetting solution, dissolve 30 grams of trichloroacetic acid in isopropanol and make the volume up to 100 cc. This solution must be used with care, and contact with the skin should be avoided.

PROCEDURE

Wet a 1-cm. section of the test paper with the corresponding impregnating solution and hold it in a parallel position about 5 mm. from the surface of the heating element, which is pressed against the rubber sample. If evolution of vapor is sufficiently rapid, an adequate test is obtained in 4 to 6 seconds. In testing for natural rubber and GR-S, it is desirable to continue the test until the color which is formed can be seen through the back of the paper. The hue should be judged from the appearance of the paper facing the heating element. Charring the paper and overdeveloping the color should be avoided.

The reactions which are obtained from the various polymers, using the three types of indicator papers, are summarized in Table III.

DETECTION OF MIXTURES

A general procedure for the detection of mixtures requires more specific and detailed methods than those described. However, by careful observation of the results obtained by the pyrolysis procedure, it is frequently possible to detect deviations from normal behavior which will indicate the need for a more complete analysis.

Compounds containing natural rubber and GR-S in approximately equal amounts yield green-blue reaction products which are readily distinguishable from those of the pure materials. The test is not applicable to compounds in which the minor constituent comprises less than 25 to 35 per cent of the total polymer, as the colors are difficult to match and may be stimulated by the

presence of other materials. Natural rubber reclaims produce green-blue to blue colors which differ in appearance from those obtained on compounds based on crude rubber and may suggest the presence of GR-S as the minor components of a mixture. In such cases more specific tests must be applied to make identification certain.

Experiments on samples of known composition indicate that the Weber test[1] can be used to detect natural rubber in the presence of GR-S, Neoprene, and Perbunan. Positive reactions are obtained from natural rubber (Hevea), guayule, and balata. A violet color of low intensity is obtained on testing polyvinyl acetate. Natural rubber reclaim gives a red-violet color which is distinguishable from the opaque blue-violet obtained on testing samples containing crude rubber.

A qualitative test for GR-S in the presence of natural rubber is described in a recent publication[3]. The extracted sample is nitrated, reduced, and diazotized. The formation of a crimson azo dyestuff on coupling with β-naphthol indicates the presence of GR-S, or more generally, the presence of a polymer containing aromatic groups. The method is of value whenever a laboratory procedure can be used, and serves to establish the presence of GR-S in small amounts.

Perbunan is readily detected in the presence of Neoprene by the reaction with *p*-dimethylaminobenzaldehyde, as the intense red color masks the yellow-green of the Neoprene (Figure 2). On testing Neoprene-ILS, which contains both nitrile nitrogen and chlorine, positive tests for both groups are obtained in the initial pyrolysis procedure. The acid-base indicator confirms the presence of an acidic substance in the decomposition products, while the aldehyde reaction indicates the presence of a nitrogenous polymer. Perbunan can also be satisfactorily detected in mixtures by the copper acetate-benzidine reaction or by the Prussian blue test[1].

The presence of Neoprene as a minor component in mixtures is established by use of the Beilstein test when the low concentration and the presence of alkaline compounding ingredients obscure the normal acid reaction.

A copper wire is heated to redness and touched to the sample. If, on reheating, a brilliant green is imparted to the flame, a compound containing chlorine is present. Polyvinyl chloride and other nonvulcanizable polymers can be distinguished from Neoprene by extracting the sample with acetone and examining the residue obtained on evaporating the solvent for the presence of a resinous material of high chlorine content. Neoprene is not removed from vulcanized compounds by acetone extraction. This procedure is of general value for distinguishing curing from noncuring polymers in mixtures. The choice of solvent and method of isolating the extractible polymer from the residue must be decided in each case from a knowledge of the properties of both components.

DISCUSSION

The pyrolysis procedure has been applied to compounds prepared in the laboratory and to a large number of commercial samples, including most of the standard reclaims. The color reactions give more consistent results than the specific gravity tests[1] on unextracted samples, and vary less widely with experimental conditions. When circumstances make it possible, it is preferable to make the tests on extracted samples, but in many cases this step is unnecessary. The density ratio values (Table II) illustrate the normal variations between

extracted and unextracted samples. In most cases the differences are too small to be detected visually, and are less than those obtained on testing extracted samples containing the same polymer taken from different compounds.

The best evidence for the reliability of the test is provided by the successful testing of reclaimed rubbers, for they may be regarded as composite samples of the different types of compounds used within a commodity group. In addition, they are subjected to a devulcanizing process in which considerable amounts of softening agents are added, and which is accompanied by partial degradation of the original polymer.

A number of materials which are commonly found in rubber products yield pyrolyzates which react with *p*-dimethylamino-benzaldehyde (Table IV).

TABLE IV

COLOR REACTIONS OF NONRUBBER MATERIALS

Material	Initial Test	After Dilution and Heating
Solvenol	No reaction	No reaction
Mineral rubber	Yellow	Pale green yellow
BRT-7	Orange	Red
Asphalt	Pale yellow green	Pale yellow green
Pine tar	Yellow	Green
Cumar-EX	No reaction	Green
Polyvinyl alcohol	Yellow green	Pale yellow green
Cellulose	No reaction	Pale orange

While color reactions are obtained on many of them, in general the intensities are of the same order or less than those obtained from the polymers, and as in the case of natural rubber—GR-S mixtures, a considerable amount of the minor component must be present before a noticeable alteration in hue is obtained.

The pyrolysis procedure is preferred for general testing purposes. However, the spot reactions are more convenient when it is necessary to test a large number of samples to confirm the presence of a particular polymer type, such as in the segregation of mixed natural rubber—GR-S consignments, or in the separation of Perbunan and Neoprene-ILS scrap from Neoprene before reclaiming. In some cases it is convenient to use the spot tests for Butyl and Neoprene in conjunction with the pyrolysis procedure, and eliminate the pH tests made with Solution II. The spot test for natural rubber and GR-S gives well defined results on compounds prepared from pure-gum stocks, and can be used in most applications. When the sample is based on a mixture of the two polymers, the intermediate color which is obtained is more easily distinguished when the reaction is carried out in solution. However, if the sample contains a large amount of cellulose which cannot be separated mechanically before making the test, the spot reaction should be used, as the aqueous products which are formed on decomposition of the cellulose retard the development of the color in alcohol solution.

The tests described provide a rapid, accurate method for the identification of the principal polymer types likely to be present in commercial rubber samples. When mixtures containing considerable amounts of both components are encountered, tests intermediate between those of the pure materials are usually obtained. In some instances a positive identification can be made on the basis of these tests alone; in others, more detailed methods of analysis must be employed.

In the foregoing discussion the reactions of the polymers have been classi-

fied under specific types which represent the most commonly used members of groups of closely related materials—for instance, the reactions which serve to classify compounds based on pale crepe are equally applicable to guayule and balata. Most of these reactions, while useful for distinguishing polymers and groups of polymers from one another, provide insufficient evidence for a fundamental proof of structure.

It is possible that the pyrolysis technique can be used for the evaluation of polymers by the application of quantitative methods to the analysis of the distillates. The radicals formed on thermal decomposition should give rise to compounds, the nature of which are predetermined by the structure and composition of the original materials. An application is illustrated in Figure 3,

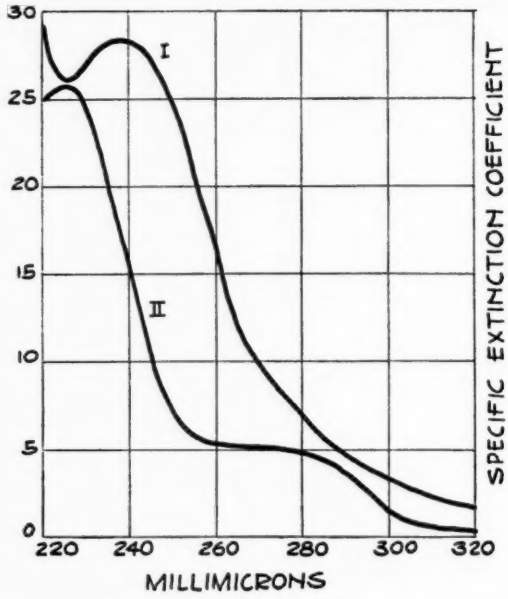


FIG. 3.—Ultraviolet Absorption Spectra of Pyrolyzates from Uncompounded Polymers in Iso-octane

I. GR-S. II. Natural rubber

in which the ultraviolet absorption spectra of the pyrolyzates from uncompounded natural rubber and GR-S are shown. The appearance of the absorption bands clearly reflects a difference in composition between the two substances. As the products formed in pyrolytic reactions usually vary with experimental conditions, it is evident that these factors must be carefully controlled before useful data can be obtained. While the optical and chemical properties of the pyrolysis products are of potential analytical interest, the application of quantitative methods is beyond the scope of this discussion.

ACKNOWLEDGMENT

The author wishes to express his thanks to W. J. S. Naunton for permission to describe the qualitative test for GR-S contained in Users' Memorandum U.9 on the "Identification and Estimation of Natural and Synthetic Rubbers".

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AN IMPROVED BRITTLE POINT APPARATUS *

F. L. GRAVES

RESEARCH LABORATORIES, AMERICAN CYANAMID AND CHEMICAL CORPORATION, STAMFORD, CONN.

In the paper "Evaluating Low Temperature Stiffness and Brittle Point in Elastomers"[1] several methods for determining the brittle points of rubber and rubberlike compounds were reviewed, and the apparatus developed in these laboratories in 1942 for this test was described in detail.

The original device represented a step toward evaluation of this property under more uniform conditions of rate and degree of deformation than had

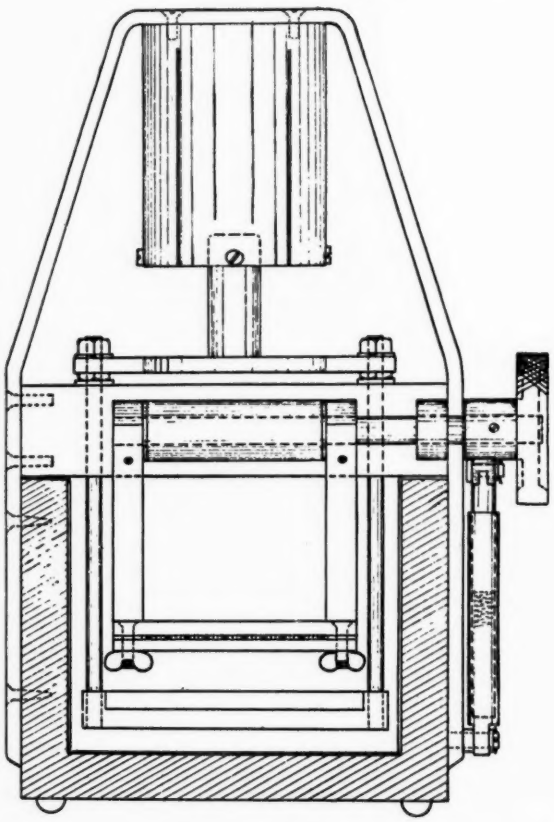

FIG. 1.—Improved Cynamid Brittle Point Apparatus—Front View—Inside Tank.

* Reprinted from the *India Rubber World*, Vol. 113, No. 4, page 521, January 1946.

hitherto been employed. The instrument consisted of a temperature conditioning bath containing a convenient specimen clamp and a spring loaded plunger mechanism designed to bend several test-pieces through an arc of 90 degrees at a high rate of deformation.

The need of a more powerful plunger action became evident when the A.S.T.M. in its method of Test D746–44T adopted as a tentative standard the impact rate of $6\frac{1}{2} \pm \frac{1}{2}$ feet per second for brittle point determinations. At a meeting of Subcommittee XXV of Committee D-11 in Cincinnati in March,

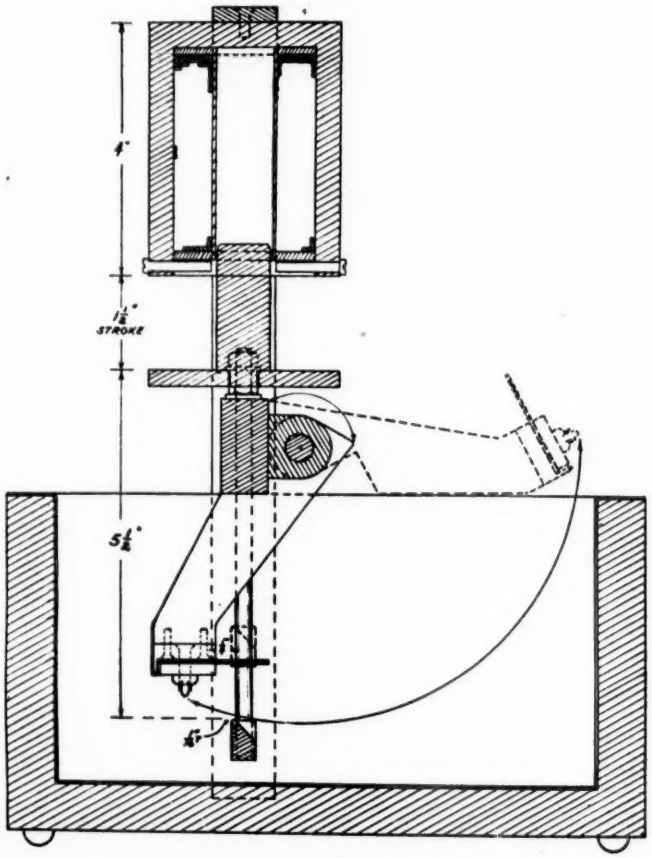

FIG. 2.—Improved Cynamid Brittle Point Apparatus—Side View—Section at Center.

1944, the use of the motor-driven striking arm developed by Kemp, Malm, and Winspear[2] was discussed, and the possibility of an A.C. solenoid as a power source for the impact blow was also proposed.

For its simplicity in design and operation the solenoid was chosen by us to replace the spring loaded plunger employed in the original apparatus. This power source has also been employed in a similar instrument developed by Bimmerman and Keen[3].

The Cyanamid brittle point apparatus combines an easily manipulated specimen holding mechanism with a sufficiently powerful solenoid to bend or break as many as ten specimens with a single impact stroke. The instrument is compact and portable and may be placed in the well of a small commercial cold air cabinet for first-order transition studies or other tests in which liquid cooling media are to be avoided.

The design of the device is shown in the accompanying sketches. (Figures 1 and 2.) A specimen clamp to accommodate up to ten T-50 test specimens is mounted on a shaft to which a compression spring locking device is attached. Clockwise rotation of the wheel at the right end of the shaft (Figure 1) brings the specimen holder out of the conditioning bath where it is automatically secured in a convenient position for rapid inspection and reloading. Counter-clockwise rotation of the control wheel lowers the loaded clamp into the bath, automatically locking the specimens as cantilever beams in a horizontal plane above the impact plunger.

Closing the circuit to the solenoid (110-volt A.C.) causes the plunger to strike the under side of the specimens at a distance of $\frac{1}{4}$-inch from the clamp, bending those which remain flexible through an arc of 90 degrees. High-speed camera studies of the plunger action against ten specimens of a GR-S tire tread

FIG. 3.

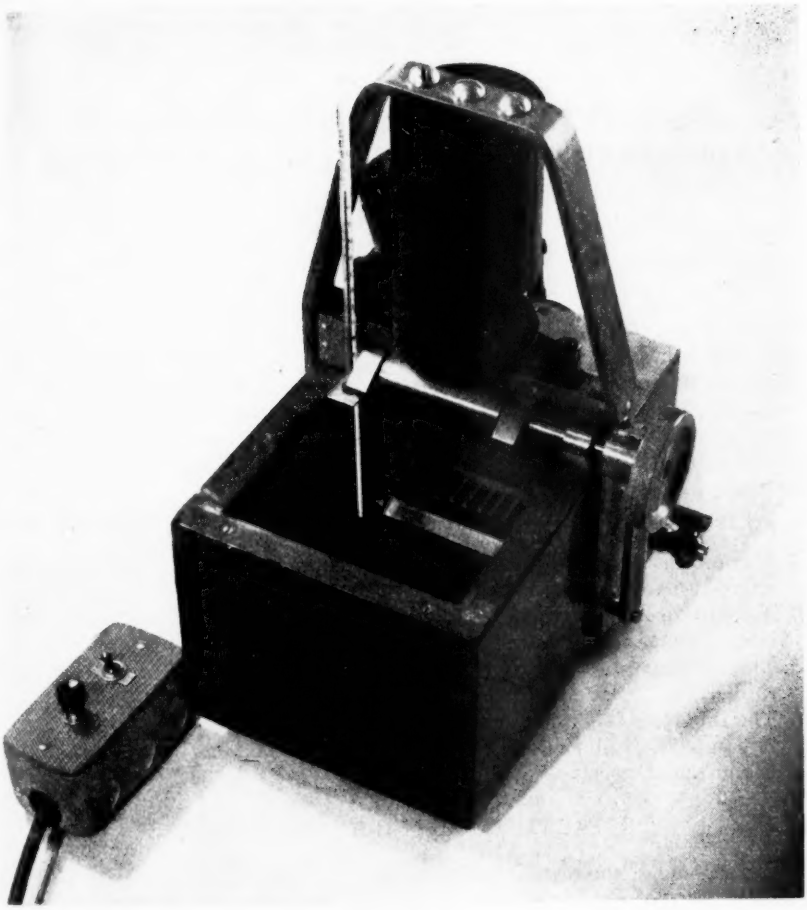

FIG. 4.

compound at 2° C above the brittle point indicated that a speed of $6\frac{1}{2} \pm \frac{1}{2}$ feet per second is attained at the moment of contact and maintained throughout the bending operation as required by A.S.T.M. for this test.

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A COMPARISON OF DIFFERENT TYPES OF RUBBER OBTAINED FROM THE SAME FIELD LATEX

G. J. VAN DER BIE

NETHERLANDS INDIES RUBBER RESEARCH INSTITUTE, BUITENZORG, JAVA

INTRODUCTION

Several comparative investigations of various types of raw rubber have been published, but most of these refer to products of different origin, hence it is not known to what extent the results depended on natural variations in the rubber. Moreover, the investigators, who prepared their own material, worked either with old latex in Europe, in the United States or in the tropics, where the work was confined to only a few types of rubber.

The present investigation was conducted with the following objects in view:

(1) A comparison of various types of commercial rubber, *i.e.*, smoked sheet, crepe and whole-latex rubber.
(2) A comparison of these rubbers with those obtained from different types of latex (or cream latex).
(3) The influence of storage of latex (cream latex) on the properties of the rubber.
(4) The influence of storage on various types of rubber.
(5) A comparison of the accelerated aging tests of Geer and Evans and of Bierer and Davis.

PREPARATION OF THE RUBBER SAMPLES

The scheme of the experiments is shown in Table 1.

Fifty liters of field latex were obtained from the experimental garden of Tjiomas; ten liters of this was coagulated and milled into sheets at Tjiomas; the remaining forty liters, after addition of ammonia, was sent to the laboratory One-half of the latter was worked up immediately; the other half was stored for 6 months. The crepe was prepared in the usual way from diluted latex (1:1) or cream (it would have been preferable to dilute the cream before coagulation to the same standard coagulation as the latex).

The whole-latex rubber was prepared by drying the latex on leveled glass plates; this required two days.

The latex was creamed in the customary way, *i.e.*, with 14 cc. of 1 per cent konnyaku-meal per 100 cc. of latex. Cream I was clarified once.

For the preparation of cream II, cream I was first diluted to about 27 per cent dry rubber content, after which it was creamed again. Cream II was clarified twice.

The samples of rubber were investigated according to the scheme shown, and the remaining samples were stored in darkness.

In June 1939 the stored latex and cream were worked according to the scheme outlined.

TABLE 1

SCHEME OF THE EXPERIMENTS

Dry rubber content	Total solids	Treatment of the latex	Type of rubber
—	—	FIELD LATEX fresh	smoked sheet
34.9	38.00	FIELD LATEX fresh, ammonia added	crepe whole-latex rubber
48.9	50.6	CREAM I fresh	crepe whole-latex rubber
47.9	48.6	CREAM II fresh	crepe whole-latex rubber
47.6	49.6	CREAM I after 6 months	crepe whole-latex rubber
31.4	35.1	FIELD LATEX after 6 months	crepe whole-latex rubber
		CREAM from matured field latex	crepe whole-latex rubber

On the latex stored in a demijohn a thick cream layer formed, and this could no longer be completely dispersed. Hence, the latex was strained through a wire-mesh sieve, thus causing a loss of coagulum; this accounts for the difference in dry rubber content and total solids of the latex before and after storage.

The creaming of the latter latex offered no difficulties, the cream being clarified in the usual way. The dry rubber content of the cream obtained was much higher than when fresh field latex was creamed.

The stability of the different latices and creams was normal. The rubber samples were analyzed according to the scheme, and the remaining samples were stored in the dark.

In March 1940 the remaining samples were investigated again. The sheet sample and all the samples of whole-latex rubber had become mouldy, whereas the samples of crepe which had been stored in the same way (that is, wrapped in filter-paper) showed no mould growth.

CHEMICAL ANALYSIS

The results of the chemical analysis of the samples are recorded in Table 2.

TABLE 2

COMPOSITION OF THE RUBBER SAMPLES

Latex	Type of rubber	% Moisture	% Ash	% Nitrogen	% Aqueous extract	% Acetone extract	% Alcoholic potash extract	Free fat acids (mg. KOH per 100 g.)	Combined fat acids (mg. KOH per 100 g.)	Copper (mg. per 100 g.)
		Fresh rubber samples, December 1938 and June 1939								
Field latex	sheet	1.18	0.38	0.60	1.38	3.09	0.40	24	15	0.35
Field with NH_3	crepe	0.67	0.19	0.49	0.27	2.33	0.86	66	83	0.26
	whole-latex rubber	3.84	1.37	0.79	3.88	2.35	0.68	29	14	0.59
Cream I	crepe	0.42	0.13	0.33	0.11	2.91	0.48	111	52	0.36
(fresh)	whole-latex rubber	3.00	0.86	0.51	0.50	3.25	0.32	33	6	0.52
Cream II	crepe	0.29	0.12	0.24	0.17	2.65	0.56	54	37	0.43
(fresh)	whole-latex rubber	2.31	0.35	0.34	0.16	2.63	0.47	49	9	0.43
Cream I	crepe	0.30	0.14	0.31	0.11	3.25	0.40	234	32	0.38
(6 months)	whole-latex rubber	2.07	0.70	0.52	1.06	3.51	0.86	257	17	0.56
Latex	crepe	0.33	0.10	0.47	0.13	3.43	0.54	269	24	0.51
(6 months)	whole-latex rubber	3.76	1.41	0.84	8.40	3.97	1.09	249	24	0.53
Cream from	crepe	0.19	0.08	0.25	0.11	2.87	0.48	200	21	0.38
old latex	whole-latex rubber	1.82	0.50	0.39	0.13	2.98	0.84	176	49	0.37
		Stored rubber samples, March 1940								
Field latex	sheet	0.68	—	0.54	0.54	2.28	0.30	28	0	—
Field with NH_3	crepe	0.72	—	0.48	0.32	1.76	0.65	55	18	—
	whole-latex rubber	3.75	—	0.73	1.50	1.50	0.29	32	15	—
Cream I	crepe	0.45	—	0.35	0.28	1.84	0.67	64	21	—
(fresh)	whole-latex rubber	2.60	—	0.48	0.53	1.47	0.30	30	4	—
Cream II	crepe	0.35	—	0.24	0.23	1.69	0.81	44	28	—
(fresh)	whole latex rubber	0.94	—	0.30	0.25	1.40	0.44	38	0	—
Cream I	crepe	0.38	—	0.29	0.18	2.76	0.44	207	33	—
(6 months)	whole-latex rubber	1.21	—	0.47	0.45	1.24	0.33	26	19	—
Latex	crepe	0.46	—	0.46	0.21	3.00	0.55	241	12	—
(6 months)	whole-latex rubber	—	—	—	—	—	—	—	—	—
Cream from	crepe	0.28	—	0.23	0.18	2.70	0.44	197	18	—
old latex	whole-latex rubber	1.69	—	0.36	0.38	1.42	0.47	40	10	—

All values except moisture, are given on the dry substance

The ash and nitrogen content, as well as the aqueous extract and the percentage of combined fat acids depends greatly on the preparation of the rubber samples, as was to be expected. During storage of cream and latex, the nitrogen contents of the corresponding rubber samples do not change; the acetone extract increases slightly and the aqueous extract and alcoholic potash extract of the whole-latex rubber and the percentage of free fat acids[1] of crepe and whole-latex rubber increases considerably.

The ash content of the crepe decreased considerably during storage of the latex; the ash content of the whole-latex rubber of the cream decreased also when the latex was stored before creaming.

During storage of the rubber samples, the nitrogen contents of the corresponding rubber samples remained the same; the content of combined fat acids decreased greatly; the acetone extract, the alcoholic potash extract and the percentage of free fat acids decreased considerably; the aqueous extracts of the samples, which originally were high, decreased considerably, but increased in the samples which originally showed low values (the decreases in the aqueous extract were likely the result of mould growth; however, the increase occurred also in the crepes, which showed no mould growth).

There are outstanding differences in the composition of smoked sheet and crepe from fresh field latex; this results from incomplete removal of serum in the preparation of sheet rubber.

About one-half of the copper was soluble in dilute acid, and accordingly was removed by coagulation in the freshly prepared rubber samples.

No changes of the copper contents occurred during storage of cream I. During storage of the latex, all the copper became insoluble in dilute acid; part of it, however, could be removed by creaming.

VULCANIZATION

Vulcanization mixture	I	II
Rubber	100	100
Sulfur	3	3
Zinc oxide	5	5
Diphenylguanidine	1	1
Aldol-α-naphthylamine	—	—

Temperature of vulcanization: 147° C

To carry out the experiments with the smallest quantity of each sample of rubber, the tensile tests were carried out on dumbbells punched from sheets 0.5 mm. thick[2].

A sheet 10 × 10 cm. (about 5 grams of rubber) was used for each time of vulcanization, and 6 dumbbells were punched from each sheet.

The mixtures were prepared on mills, and were vulcanized in an autoclave press.

The vulcanizates were not conditioned as to humidity.

Table 3 summarizes the results of the vulcanization tests.

Time of vulcanization

Crepe and smoked sheet prepared from fresh latex in general had slightly higher rates of vulcanization than that of whole-latex rubber from the same latex or cream. During storage of latex or cream, whole-latex rubber in general maintained a constant rate of vulcanization or at least only a slightly decreasing rate, whereas in every case crepe had a slower rate of vulcanization, which

was always more than (or at least the same as) that of the corresponding whole-latex rubber. This may be seen from the following results.

Preparation of the rubber samples	Without antioxidant		Containing antioxidant	
	Crepe	Whole-latex rubber	Crepe	Whole-latex rubber
Field latex (fresh)	25	30	30	30
Field latex (after 6 months)	35	30	35	35
Cream I (fresh)	25	30	20	25
Cream I (after 6 months)	35	30	30	30
Cream from old latex	30	30	30	30

On storage of the rubber samples from fresh field latex, the rate of vulcanization increased.

Tensile strength

In general whole-latex rubber had a high tensile strength. Smoked-sheet rubber had the same tensile strength as whole-latex rubber from field latex.

On storage of latex or cream, the tensile strengths of crepe and of whole-latex rubber increased, but by creaming of old latex the tensile strength of crepe remained the same as the tensile strength of crepe from fresh field latex, whereas the tensile strength of whole-latex rubber increased considerably and approached the value of the tensile strength of cream I after 6 months' storage.

The tensile strength in general decreased on storage of the rubber samples.

Modulus

There was little difference in the moduli of samples from fresh field latex. *The modulus of the crepe rubber samples increased during storage of the latex or*

TABLE 3

SUMMARY OF OPTIMUM VULCANIZATIONS

Latex	Type of rubber	Time of vulcanization (min.)	Tensile strength (kg. per sq. cm.)	Elongation at rupture (%)	Modulus at 600% elongation (kg. per sq. cm.)	Sulfur	
						combined (%)	total (%)
Mixture I, fresh rubber samples (without antioxidant)							
Field latex	sheet	25	287	822	65	1.36	2.45
Field latex, with ammonia	crepe	25	270	796	65	1.47	2.58
	whole-latex rubber	30	284	785	59	1.83	2.70
Cream I (fresh)	crepe	25	285	824	63	1.88	2.75
	whole-latex rubber	30	280	758	84	2.19	2.85
Cream II (fresh)	crepe	30	297	793	71	1.99	2.64
	whole-latex rubber	30	311	795	73	2.03	2.80
Cream I (6 months)	crepe	35	290	754	87	1.86	2.71
	whole-latex rubber	30	311	806	71	2.11	2.82
Latex (6 months)	crepe	35	280	772	85	1.98	2.73
	whole-latex rubber	30	290	781	81	2.32	2.85
Cream from old latex	crepe	30	265	815	53	1.95	2.75
	whole-latex rubber	30	303	801	61	1.96	2.79

TABLE 3.—*Continued*

Latex	Type of rubber	Time of vulcanization (min.)	Tensile strength (kg. per sq. cm.)	Elongation at rupture (%)	Modulus at 600% elongation (kg. per sq. cm.)	Sulfur	
						combined (%)	total (%)
Mixture II, fresh rubber samples (containing antioxidant)							
Field latex	sheet	25	271	794	71	1.28	2.39
Field latex with ammonia	crepe	30	264	755	79	1.44	2.44
	whole-latex rubber	30	271	805	63	1.54	2.42
Cream I (fresh)	crepe	20	274	805	61	1.86	4.65+
	whole-latex rubber	25	291	736	112	2.82	5.13+
Cream II (fresh)	crepe	20	289	779	84	1.94	4.85+
	whole-latex rubber	20	275	792	67	1.74	4.34+
Cream I (6 months)	crepe	30	274	795	68	1.93	2.81
	whole-latex rubber	30	292	795	74	1.92	2.87
Latex (6 months)	crepe	35	298	769	95	1.90	2.72
	whole-latex rubber	35	328	753	115	2.51	2.95
Cream from old latex	crepe	30	278	791	62	1.87	2.66
	whole-latex rubber	30	296	781	81	2.06	2.92
Mixture I, stored rubber samples (without antioxidant)							
Field latex	sheet	20	237	827	55	—	—
Field latex with ammonia	crepe	20	216	873	35	—	—
	whole-latex rubber	20	259	802	65	—	—
Cream I (fresh)	crepe	—	—	—	—	—	—
	whole-latex rubber	30	267	760	81	—	—
Cream II (fresh)	crepe	—	—	—	—	—	—
	whole-latex rubber	—	—	—	—	—	—
Cream I (6 months)	crepe	35	236	808	55	—	—
	whole-latex rubber	—	—	—	—	—	—
Latex (6 months)	crepe	35	232	769	75	—	—
	whole-latex rubber	—	—	—	—	—	—
Cream from old latex	crepe	25	231	919	21	—	—
	whole-latex rubber	30	297	798	78	—	—

+ Owing to an error during mixing.

cream[3]. During storage of the rubber, the modulus of the whole-latex rubber increased, whereas the modulus of the smoked sheet and crepe rubber generally decreased.

Combined sulfur

The whole-latex rubber samples had higher percentages of combined sulfur than did the crepe rubber samples.

5. ACCELERATED AGING TESTS

Aging tests were made with optimum vulcanizates by the Geer and Evans method (air at 70° C) and by the Bierer and Davis method (20 atmospheres of oxygen at 70° C).

The results are summarized in Table 4.

TABLE 4

SUMMARY OF THE ACCELERATED AGING TESTS
(Changes in percentage tensile strength)

Aging	Type of rubber	Field latex fresh (smoked sheet)	Field latex fresh with ammonia	Cream I (fresh)	Cream II (fresh)	Cream I (6 months)	Latex (6 months)	Cream from latex 6 months old
Mixture I, fresh rubber samples (without antioxidant)								
14 days Geer oven	crepe	−11	−31	− 68	− 71	− 86	− 89	− 66
	whole-latex rubber	—	−20	− 50	− 60	− 46	− 36	− 52
28 days Geer oven	crepe	−49	−68	− 96	− 95	− 96	− 97	− 97
	whole-latex rubber	—	−54	− 91	− 95	− 91	− 62	− 87
48 hours Bierer-Davis test	crepe	−38	−91	−100	−100	−100	−100	−100
	whole-latex rubber	—	−70	− 85	− 93	− 62	− 48	− 55
Mixture II, fresh rubber samples (containing antioxidant)								
14 days Geer oven	crepe	+11	+ 5	− 23	− 26	− 41	− 47	− 30
	whole-latex rubber	—	+ 3	− 29	− 29	− 25	− 14	− 24
28 days Geer oven	crepe	−21	−27	− 71	− 58	− 79	− 94	− 70
	whole-latex rubber	—	−27	− 81	− 61	− 54	− 38	− 51
48 hours Bierer-Davis test	crepe	−13	−15	− 2	− 28	− 40	− 42	− 26
	whole-latex rubber	—	− 8	− 24	− 13	− 22	− 23	− 22
Mixture I, stored rubber samples (without antioxidant)								
14 days Geer oven	crepe	−13	− 7	—	—	− 72	− 89	− 58
	whole-latex rubber	—	−29	− 54	—	—	—	− 34
28 days Geer oven	crepe	−51	−40	—	—	− 94	− 92	− 93
	whole-latex rubber	—	−61	− 88	—	—	—	− 73
48 hours Bierer-Davis test	crepe	−35	−38	—	—	−100	−100	−100
	whole-latex rubber	—	−31	− 67	—	—	—	− 59

The quantity of the stored rubber samples has not been sufficient for an aging test in the mixture containing antioxidant.

Mixture without antioxidant

(1) Smoked-sheet rubber deteriorated least of all. In general whole-latex rubber aged less rapidly than did crepe rubber; an exception was rubber from fresh field latex after 6 months' storage.

(2) Creaming increased the deterioration.

(3) During storage of field latex, degradation of the crepe increased considerably, whereas degradation of whole-latex rubber was relatively slight. On storage of cream few changes occurred.

(4) During storage of the rubber samples few or no changes occurred; an exception was the samples from fresh field latex in the Bierer-Davis test.

(5) The degradation resulting from the Bierer-Davis method about equalled the degradation from 28 days in the Geer-Evans oven for the samples from fresh field latex; the values for smoked-sheet rubber were between those of 14 and 28 days Geer-Evans test.

Mixture containing an antioxidant

By adding an antioxidant, deterioration was considerably retarded.

(1) The difference between smoked sheet and the other types of rubber was minimized. Only with the old latices was a difference in the deterioration of crepe and whole-latex rubber still evident.
(2) The influence of creaming was the same as mentioned for the mixture without an antioxidant.
(3) Here also the deterioration of crepe increased considerably during storage of field latex, whereas the deterioration of whole-latex rubber was relatively slight.
(4) The deterioration by the Bierer-Davis method was reduced to the same extent as that of 14 days in the Geer-Evans oven.

A comparison of Tables 2 and 4 indicates that there is no simple correlation between the copper contents of rubber samples and the aging properties of their vulcanizates; for instance, the whole-latex rubber samples generally showed good durability, notwithstanding their high copper contents. It is to be expected that this correlation, if present, would be a complicated one, when it is kept in mind that durability is governed by harmful components, *e.g.*, copper, as well as by favorable components, *e.g.*, natural antioxidants. Furthermore the author is of the opinion, based on other experiments, that not only is the percentage of copper important, but also the manner of combination of this copper; hence the idea of "active copper" should probably be introduced.

REFERENCES

[1] Although the method used for determining the percentage of free and combined fat acids is not altogether without faults, the values obtained are nevertheless recorded, since they are highly instructive.
[2] See *Arch. Rubbercultuur* **24**, 46 (1940).
[3] The question whether this is a result of continuous polymerization of the rubber or a change in the composition and the quantity of the interface components must be answered by further experimentation.

NATURAL RUBBER FROM RUSSIAN DANDELION*

RODERICK K. ESKEW

EASTERN REGIONAL RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE, PHILADELPHIA, PA.

A great deal has been published during the past three years regarding the various sources of natural rubber which have been called upon to supplement this nation's stockpile and to meet those special needs for which commercial synthetic rubbers are not entirely satisfactory. We have read of wild rubbers being brought in under great difficulty from Central and South America; of the 32,000 acres of guayule grown by the government, largely in California, and now nearly ready for harvest; and of the large experimental plantings of *Cryptostegia* in Haiti. Almost nothing, however, has appeared regarding a plant which is known to be potentially rich in high-grade rubber and which has been extensively cultivated outside this country. This is the Russian dandelion, or *Taraxacum kok-saghyz*.

In the course of a systematic investigation instituted in Russia in 1929 to determine the possibilities of producing natural rubber in that country, the *kok-saghyz* was found near Tien Shan, Kazakstan, near the border of China. By 1932 more than 2,000 acres of this plant were under cultivation in Russia, and it is reported that at the time of the German invasion of Russia approximately 200,000 acres of *kok-saghyz* had been planted for the production of rubber.

Shortly after the tragedy at Pearl Harbor, the United States Government started negotiations with Russia to obtain *kok-saghyz* seed. These eventuated in the arrival in Washington on May 8, 1942, of two gunny sacks of seed, flown from Kuibyshev. On the same day that the seed arrived, some of it was repackaged and distributed by air to various points in the United States, where more than 60 indicator plantings were established through coöperation with state agricultural experiment stations.

It was shortly before this time that the Emergency Rubber Project was authorized by Congress. It was "An Act to provide for the planting of guayule and other rubber-bearing plants and to make available a source of crude rubber for emergency and defense uses. . . ." The responsibility for the Emergency Rubber Project was delegated by the Secretary of Agriculture to the Forest Service. The Forest Service in turn called on other bureaus in the Department to assist in certain phases of the work. The task of carrying out agronomic and plant improvement research was assigned to the Bureau of Plant Industry, Soils, and Agricultural Engineering. The Bureau of Agricultural and Industrial Chemistry was charged with the responsibility of developing methods for recovering the rubber from these plants, for determining the technical feasibility of such methods by pilot-plant operations, for evaluating the rubber obtained, and for determining the economic factors involved in rubber recovery. These responsibilities were, in turn, delegated to the Eastern

* Reprinted from the *India Rubber World*, Vol. 113, No. 4, pages 517–520, January 1946. This is Paper No. 11 in a series on "Natural Rubber from Domestic Sources".

Regional Research Laboratory at Philadelphia. Thus, when the first *kok-saghyz* roots were harvested in the Fall of 1942, they were shipped to the Laboratory at Philadelphia for rubber-recovery studies.

In spite of the late planting of the seed and the unsatisfactory nature of some of the planting sites, sufficient roots were obtained to make it possible to work out on a batch pilot-plant scale a comparatively simple process for recovering the rubber. A large-scale continuous pilot-plant unit was designed and erected at the Philadelphia Laboratory, and during the Winter of 1943 and 1944 a sufficient quantity of rubber was produced to permit its commercial evaluation. The roots for these large-scale experimental operations were derived largely from more than 600 acres of *kok-saghyz* planted by the Forest Service, principally in Michigan and Minnesota.

Analysis of typical one-season *kok-saghyz* plants showed that more than 90 per cent of the rubber is in the form of latex in interconnectind ducts in the root itself. The remainder is in the crown and leaves of the plant, which constitute about 25 per cent of its dry weight. This leaf and crown fraction, however, is rich in pectin, containing nearly 40 per cent of the total pectin in the plant. Since pectin interferes with rubber recovery, the tops were mechanically cut off in the field just before harvesting. This practice also reduces the bulk to be handled in the factory.

The rubber-recovery process described here thus applies only to the roots of *kok-saghyz*. Individual *kok-saghyz* roots having as much as 23 per cent rubber hydrocarbon on the dry basis have been grown in this country. Such a high rubber content, however, is exceptional. Most of the roots processed in the pilot plant contained between 5 and 10 per cent rubber hydrocarbon on a dry basis. The roots are also rich in carbohydrates; the amount depends, among other things, on the time of harvest; it ranges from 10 per cent in roots harvested in the spring to 45 per cent in fall-harvested roots.

Before discussing the recovery process for *kok-saghyz* rubber, it is necessary to give some consideration to the localities in which the roots may be grown and the seasons of harvesting. Although much remains to be done toward perfecting methods for growing *kok-saghyz* of high rubber content and high yields per acre, it has been grown experimentally during the winter months in certain parts of Florida and during the summer in the Red River Valley of Minnesota, in certain sections of Michigan, Wisconsin, and Montana.

For reasons of simplicity the following discussion is based on probable growing conditions in Minnesota or Michigan. It is assumed that the seed would be planted in the field as early as possible in the spring, preferably before June first. Harvesting of approximately 50 per cent of the roots planted would take place between October 15 and November 15. The remaining roots would be left in the ground until the following spring and would be harvested as nearly as possible between April 15 and May 15, with the next seeding following immediately.

Roots left in the ground during the winter generally increase percentagewise in rubber, even when harvested early the following spring. This condition is undoubtedly due in part to a corresponding loss of carbohydrates resulting from renewed top growth.

To preserve the carbohydrates during storage of harvested roots, the full six months' supply harvested in the fall, and a similar quantity harvested in the spring, would have to be dried during each harvesting period. The roots could be washed by simple devices already worked out for field operations. They could sen be spread on the ground to a depth of approximately one foot

and left to dry, with occasional turning if necessary, to as low a moisture content as weather conditions would make possible. This practice is necessary to minimize the drying capacity that would be required in a factory drying roots immediately after washing; such roots contain about 85 per cent moisture.

After drying, some roots would go immediately into process, and the remainder would be baled for storage.

RUBBER-RECOVERY PROCESS

The first step of the process consists in countercurrently leaching the dried roots in hot water to remove the carbohydrates. This produces a solution which can be fermented directly to alcohol. A small amount of soda ash is used during leaching to soften the roots. The leached roots, now only about 55 per cent of their original dried weight, are given a short pebble milling in water to disperse the softened plant tissue and to roll together the fine filaments of rubber. By diluting this slurry and screening it, 65 per cent of the remaining solids are eliminated, leaving largely rubber and adhering root skins. A second short pebble milling with water disengages the root skins from the rubber, and the two are separated by a subsequent flotation step wherein the rubber floats and the plant debris (bagasse) sinks. A final washing of the rubber on a vibrating screen removes further traces of plant material. After being centrifuged to remove excess water, the rubber is mixed with an antioxidant and then dried in a through-circulation continuous drier. It is then baled and boxed in the conventional manner. A flow sheet of the process is shown in Figure 1.

Root Drying and Storage.—Freshly washed roots or roots which have been partly field dried can be satisfactorily dried to the desired final moisture of approximately 15 per cent in a continuous through-circulation belt-type drier at temperatures up to 200° F, preferably with the relative humidity maintained at approximately 10 per cent.

The dried roots are baled and stored. They may be kept for six months or more without any change in the quantity or quality of recoverable rubber. Some loss in carbohydrates can be anticipated, however, when storage is continued beyond three or four months.

Leaching.—Leaching is carried out countercurrently in a battery of 10 to 12 tanks, using water at 200–212° F containing about 0.1 per cent soda ash. The function of leaching is threefold:

(1) When conducted countercurrently on fall-harvested roots, it removes the carbohydrates and recovers them in such a concentration as to provide a byproduct material fermentable to alcohol or to lactic acid.

(2) It reduces the dry weight of material going to the rubber-recovery system by eliminating soluble solids.

(3) The soda ash used in the early stages of leaching softens the root and facilitates pebble milling.

Milling and Screening.—Although rubber can be isolated from leached *kok-saghyz* roots by a pebble-milling process alone, it is much simpler and more economical to intersperse a dilution and a screening step between two continuous pebble-milling operations. If rubber were isolated by milling alone, the total milling time would be three or more times as great as that required for two-stage milling with intermediate dilution and screening.

In the primary milling operation, the object is to roll together the coagulated filaments of rubber and to disperse plant material, particularly the softened pulpy portions of the roots, so that on dilution they can be eliminated by

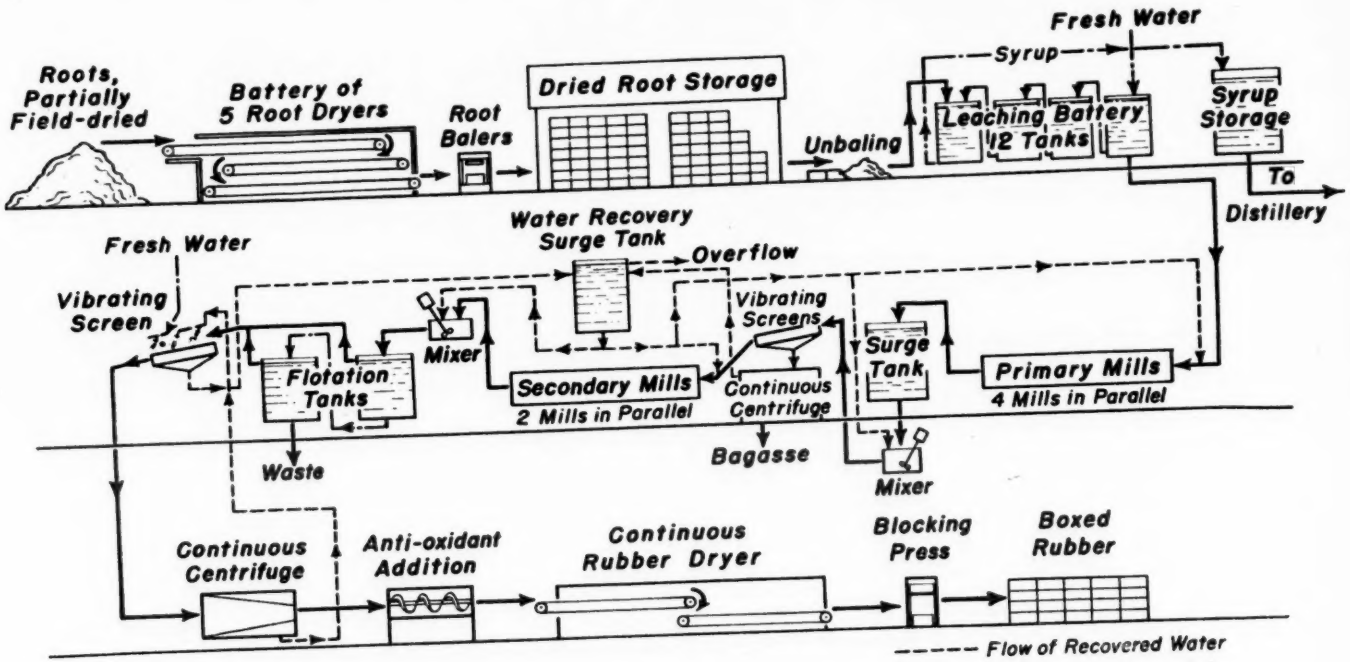

FIG. 1.—Flow Diagram for Kok-saghyz Factory—10 Long Tons of Rubber Per Day.

screening. This can ordinarily be accomplished by milling for 15 minutes in a continuous pebble mill with a ratio of 20 parts of water to one part of solids. The temperature of the mill slurry is maintained at approximately 100° F by heating the water going into the mill. This elevated temperature softens plant tissues and reduces the consistency of the slurry, thereby facilitating milling.

The completeness of primary milling can be judged by examining the web-like rubber masses emerging from the mill. When these are stretched and examined under low-power magnification, secondary phloëm can be readily observed. Primary milling should be carried to the point where the web of rubber becomes flattened and, when stretched, reveals almost complete elimination of secondary phloëm. At this stage approximately 50 per cent of the total rubber floats when the slurry is diluted to about 100/1.

About 65 per cent of the root solids can be removed by screening the slurry from the primary mill after diluting it with 100 parts of water to one part of solids. A twofold purpose is accomplished by this operation. First, the subsequent milling load is reduced by 65 per cent, and furthermore less plant material remains to contaminate the rubber. The screening operation is a very important step, and unless it eliminates at least 60 per cent of the solids, secondary milling is adversely affected, and a greatly increased milling time is necessary to cause the rubber to float. The factors affecting good screening are: (1) kind of roots, (2) effectiveness of leaching and proper control of pH during leaching, (3) completeness of primary milling, (4) slope, stroke, mesh, and weave of screens, and (5) rate of feed to the screens. The water passing through the screens contains approximately 0.6 per cent of plant material. It can be clarified in a continuous centrifuge, the water reused, and the solids recovered if they prove to have by-product value.

Since most of the material passing over the screen is rubber and adhering root skins, the function of secondary pebble milling becomes one of detaching fragments of root skins so that they may be eliminated in a subsequent flotation step. Secondary milling is ordinarily carried out for about 22 minutes at a water to solids ratio of 22:1; the temperature of the slurry is maintained at about 75° F. Higher temperatures tend to soften the rubber, resulting in the formation of balls and entrapment of foreign material. The yield of rubber in the recovery process depends on how effectively it can be floated away from plant debris. Since its floatability depends on the degree to which nonrubber components have been eliminated, the completeness of secondary milling is judged by how completely the rubber floats when a sample of the slurry from the mill is diluted with a large excess of water.

Flotation.—The flotation step, which comes immediately after the secondary milling, makes it possible for the rubber to float away from the plant debris, which sinks. The effluent slurry from the secondary pebble mill, diluted to about 100 parts of water per one part of solids, is introduced at the center and beneath the liquid level in a continuous flotation tank. Because some of the plant materials sink very slowly, the rate of slurry feed to the flotation tanks is relatively slow. The rubber is skimmed continuously from the surface of the tank by slow-moving blades that dip about two inches below the level of the liquid. At the bottom of the same shaft is a revolving scroll, which continuously moves the debris to the discharge outlet at the center of the tank. It is pumped from this outlet to a secondary flotation tank, designed exactly like the first, where any rubber entrapped in the sediment is freed to float. Two tanks in series should recover practically all the rubber if secondary milling

has been properly performed. Otherwise undermilled rubber, which does not float, is lost in the bagasse.

The floated rubber is rinsed with water sprays on a vibrating screen preparatory to drying.

Rubber Drying.—Because of the physical state in which *kok-saghyz* rubber is recovered, it lends itself readily to rapid drying at relatively high temperatures without deterioration. Before drying, it is desirable for reasons of heat economy to free the rubber of as much water as possible by centrifuging. The moisture content can be reduced to between 40 and 48 per cent without causing the rubber to stick together if the centrifugal force is kept below 100 times that of gravity.

To prevent the rubber from being degraded during drying and to enhance the physical properties of the vulcanizate, it is customary to add an antioxidant to the dewatered rubber. 4-4′-Diaminodiphenylmethane is an effective agent, and it is customarily added in the form of an aqueous emulsion, which is sprayed on the rubber. A sufficient quantity is added to give a concentration of approximately 0.45 per cent on the dry-rubber basis.

The rubber is dried in a continuous through-circulation belt-type drier at a temperature of approximately 200° F. The time required is about 45 minutes. *Kok-saghyz* rubber, when dried in this manner, has better physical properties than when dried slowly under vacuum. The rubber is baled and boxed in the conventional manner.

PHYSICAL AND CHEMICAL PROPERTIES OF KOK-SAGHYZ RUBBER

Rubber produced by the foregoing process had the following average analysis:

	%
Rubber hydrocarbon (by bromination)	80.5
Benzene-insoluble material (by direct determination)	12.5
Acetone-soluble material (by difference)	7.0

The benzene-insoluble material can be reduced to 5 per cent or less by an additional pebble-mill scrubbing, but unlike the benzene-insoluble material in guayule rubber, which is in part fibrous and woody and hence harmful, this fraction in *kok-saghyz* rubber is unobjectionable. It consists principally of finely divided, soft, inert material, which acts like so much filler.

Although the percentage of acetone-soluble material of *kok-saghyz* rubber is high, as compared with *Hevea*, this fraction is not resinous, nor does it contribute objectionable properties such as softness or excessive tackiness. It consists largely of an unidentified white crystalline substance dissolved in the rubber.

In testing the physical properties of *kok-saghyz* rubber, both the A.C.S. and the A.C.S. alternate formulas give curing curves which are too flat for good evaluation. Satisfactory results were obtained by curing at 274° F, and adding 0.1 per cent diphenylguanidine to the modified A.C.S. formula. The physical test data given below are therefore based on the following formula:

	Parts
Rubber	100
Zinc oxide	6
Stearic acid	4
Mercaptobenzothiazole	0.5
Diphenylguanidine	0.1
Sulfur	3.5

A.S.T.M. recommendations were adhered to with the exception that compounding was done on a 4 × 8 inch mill. Figure 2 shows a typical tensile strength-curing time curve for *kok-saghyz* rubber containing 0.4 per cent of 4-4′-diaminodiphenylmethane. Some of the physical properties are as follows:

	Tested 24 hours after cure	Raw rubber aged before compounding (48 hrs. in O_2 at 70° C & 300 lbs. per sq. in.)
Cure at 274° F	20 minutes	35 minutes
Optimum tensile	3420 lbs. per sq. in.	3100 lbs. per sq. in.
Modulus at 600%	1560 lbs. per sq. in.	1930 lbs. per sq. in.
Ultimate elongation	750%	690%
Hardness (durometer)	43	44

When *kok-saghyz* rubber is compounded with an appropriate antioxidant, the aging properties of the vulcanized rubber compare favorably with those of *Hevea*. Figure 3 shows the changes in tensile strength and elongation which result when the vulcanizate from *kok-saghyz* rubber, compounded according to the foregoing formula plus 0.25 part of 4-4′-diphenylphenylenediamine as an antioxidant, is aged under the very severe conditions of 72 hours in oxygen at 70° C and 300 per sq. in. pressure.

Laboratory tests on a new rubber are obviously of limited significance. Consequently the Department of Agriculture made arrangements with two large rubber companies to fabricate, in factory equipment, tires made entirely from *kok-saghyz* rubber produced in pilot-plant operations at the Eastern Regional Research Laboratory.

The B. F. Goodrich Co. fabricated and tested 6:00-16 four-ply passenger car tires. The road tests were made with 30 per cent overload and an operating speed of 60 miles an hour. Their report on this work states in part:

"1. Russian Dandelion Rubber is the most promising substitute for natural rubber[1] which has thus far become available. This statement is based on a general rating of four materials as substitutes for natural rubber:

"(a) Russian dandelion rubber.
"(b) GR-S.
"(c) *Cryptostegia* rubber.
"(d) Guayule.

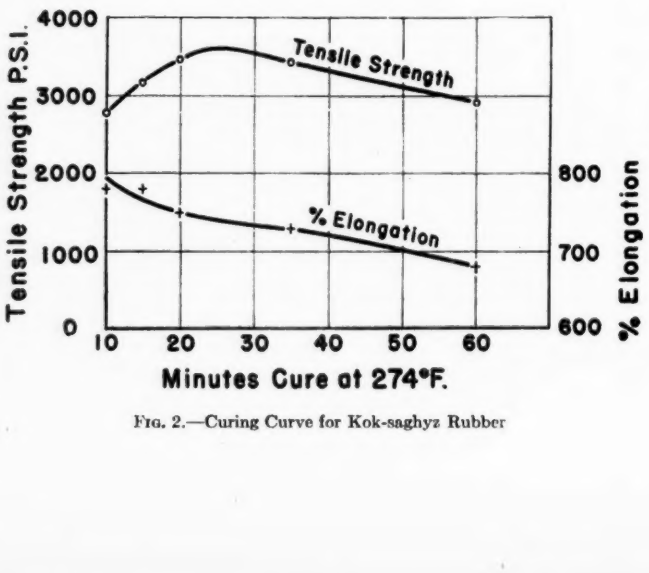

FIG. 2.—Curing Curve for Kok-saghyz Rubber

"Dandelion rubber is superior to GR-S in physical characteristics, in factory processing, in building tack, and in most tire performance characteristics.

"Dandelion rubber is superior to guayule in building tack. Guayule cements used as tackifying spreads on the carcass plies of GR-S tires produce unsatisfactory building characteristics. A Russian dandelion cement used similarly produces building characteristics equal to those produced by natural rubber cements.

"2. Russian dandelion rubber in tires is superior to GR-S and approaches the performance of natural rubber in the following characteristics:

"(a) Tread wear, on the road.

"(b) Tread crack growth, on the road

"(c) General performance, on the road.

"(d) Tread crack growth, on the indoor machine.

"(e) Tread tensile strength, at R.T. and 212° F.

"(f) Carcass ply-adhesion.

"Russian dandelion rubber in tires gives performance equal to that of GR-S and of natural rubber on the carcass separation test on the indoor machine."

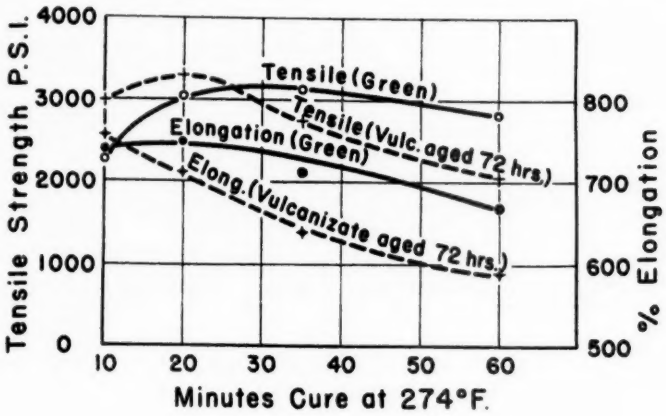

FIG. 3.—Aging of Kok-saghyz Vulcanizate

United States Rubber Co. made and tested 9:00-20/10 rayon-cord truck tires and subjected them to road tests at between 45 and 55 miles per hour with loads up to 50 per cent above normal load. Their report states in part:

"By far the most interesting fact is that *kok-saghyz* carcass ran extremely well under severe conditions, and we should be greatly pleased if we had a large supply of *kok-saghyz* available now for use in the carcass."

These comments by experts in the rubber industry leave no doubt as to the high quality of *kok-saghyz* rubber.

THE COST OF KOK-SAGHYZ RUBBER

We have stated that *kok-saghyz* can be satisfactorily grown in this country, that it contains a relatively high-grade rubber, that this rubber can be isolated by a practical process, and that it can be satisfactorily fabricated into high-grade tires. The question then arises, What will *kok-saghyz* rubber cost? This cannot be answered at present, since the largest factors in the final cost

of rubber, that is, the cost of growing the roots and the yield of rubber per acre per year, could not be adequately determined in the short time available for study. We can, however, make a reasonable estimate of the average cost of producing *kok-saghyz* rubber from roots of an assumed rubber content delivered to the factory.

Assuming a rubber hydrocarbon content on a dry basis of 10.0 per cent in fall-harvested roots and 13.4 per cent in spring-harvested roots, the estimated cost of producing one pound of *kok-saghyz* rubber would be approximately 11.7c; a credit for the fermentable carbohydrates of 2.5c per pound of rubber would result in a net cost of 9.2c. This is based on the harvesting cycle previously described in this article, and includes amortization and all other costs except that of growing, harvesting, and transporting roots to the factory. A factory producing 10 long tons of *kok-saghyz* rubber per day and operating 300 days per year would serve a planting area of approximately 40,000 acres and would cost about $1,800,000.

The foregoing assumptions are fairly conservative. Given sufficient time for breeding and selection studies, a rubber hydrocarbon content on a dry-root basis of 15 per cent for fall-harvested roots and 19.5 per cent for spring-harvested roots might reasonably be anticipated; this would reduce the factory cost of producing a pound of rubber from 9.2 to about 7.4c. Such an increase in rubber content would likewise reduce the field costs per pound of rubber.

As already pointed out, *kok-saghyz*, among other rubber-bearing plants, was included in the Emergency Rubber Project "to make available a source of crude rubber for emergency and defense uses". By 1944, however, it became apparent that "while the experimental data indicated that *kok-saghyz* holds promise of significant amounts of high-grade rubber after improvement by selection and breeding, it could not contribute sufficient quantities of rubber to meet emergency war requirements"[2].

Hence the Emergency Rubber Project work on *kok-saghyz* was terminated on June 30, 1944. However the Bureau of Plant Industry, Soils, and Agricultural Engineering, in its regular Rubber Plant Investigations' work, is continuing on a limited scale the selection and breeding of high rubber-bearing strains of *Taraxacum kok-saghyz* and its cognates *T. megalorrhizon* (*krim-saghyz*), and *Scorzonera tau-saghyz*.

It is estimated that in time the yield of rubber per acre per year from the best of these Russian dandelionlike plants should equal or exceed that from guayule. If this be true, we might then have an annual crop which in an emergency could be expanded rapidly to yield significant quantities of high-grade natural rubber.

REFERENCES

[1] Wherever "natural rubber" is mentioned in this quoted excerpt, commercial grades of estate rubbers are indicated. Kok-saghyz, Cryptostegia, and Guayule are all natural rubbers.

[2] Report of the special subcommittee of the House Committee on Agriculture, Jan. 2, 1945, House of Representatives Report No. 2098.